An assessment of skin sensitisation by the use of epoxy resin in the construction industry

Prepared by **TWI Ltd**
for the Health and Safety Executive 2003

RESEARCH REPORT 079

An assessment of skin sensitisation by the use of epoxy resin in the construction industry

S M Tavakoli
TWI Limited
Granta Park
Abington
Cambridge
CB1 6AL

Epoxy resins are one of the most important and widely used types of polymeric systems. The range of uses of epoxy resin systems includes adhesives, paints and coatings, sealants, inks, fillers, reinforced polymer composites and varnishes. It is known that epoxy resins can cause skin sensitisation and photosensitisation. Hands, arms, face and throat skin sensitisation have been reported with epoxy systems. The adverse reaction caused by an epoxy system may be due to the base epoxy resin, curing agents, diluents or other constituents in epoxy formulations. The Health and Safety Executive (HSE) has been concerned about epoxy resin sensitisation problems particularly in the construction industry where use of protective clothing or environment is less common or practical. HSE commissioned TWI to carry out a project to study skin sensitisation due to epoxy resins, particularly in the construction industry.

The main objectives of this project were to carry out a literature and industrial survey and to review information available on skin sensitisation due to the use of epoxies, particularly in the construction industry

This report and the work it describes were funded by the HSE. Its contents, including any opinions and/or conclusions expressed, are those of the authors alone and do not necessarily reflect HSE policy.

HSE BOOKS

First published 2003

ISBN 0 7176 2675 X

CONTENTS

EXECUTIVE SUMMARY

Background

Epoxy resins are one of the most important and widely used types of polymeric systems. The range of uses of epoxy resin systems includes adhesives, paints and coatings, sealants, inks, fillers, reinforced polymer composites and varnishes. It is known that epoxy resins can cause skin sensitisation and photosensitisation. Hands, arms, face and throat skin sensitisation have been reported with epoxy systems. The adverse reaction caused by an epoxy system may be due to the base epoxy resin, curing agents, diluents or other constituents in epoxy formulations. HSE has been concerned about epoxy resin sensitisation problems particularly in the construction industry where use of protective clothing or environment is less common or practical. HSE commissioned TWI to carry out a project to study skin sensitisation due to epoxy resins, particularly in the construction industry.

Objectives

The main objectives of this project were to carry out a literature and industrial survey and to review information available on skin sensitisation due to the use of epoxies, particularly in the construction industry.

Approach

Literature and industrial surveys were conducted to identify the most relevant information on epoxy resin sensitisation. Up to 53 relevant publications were reviewed. The review included the basic chemistry of epoxy resins and skin sensitisation due to various constituents of epoxy formulations. The skin sensitisation to epoxies in the construction industry was also reviewed. The most effective methods of reducing or preventing sensitisation were also described. The industrial survey included contact with construction companies and other organisations.

Concluding Remarks

As a result of the literature review, the main constituents in epoxy resin systems responsible for skin sensitisation were identified. It was shown that the reactive constituents of base resin, curing agents, diluents etc are responsible for skin sensitisation to epoxy resins used in the construction industry, either singly or in combination. A number of protective measures including use of effective protective clothing, alternative materials, mixing and dispensing procedures and safe handling of epoxy resins have been recommended.

1. INTRODUCTION

Epoxy resins are one of the most important and widely used types of polymeric systems. The variety of uses for epoxy systems includes: paints and coatings, adhesives, sealants, inks, fillers, reinforced polymer composites and varnishes. It has been known for many years that epoxy resins can cause skin sensitisation and photosensitisation. Eye, nose and throat sensitisation has also been reported when epoxy resins are being used. The adverse reaction caused by an epoxy formulation may be due to the base epoxy resin, curing agents, diluents, fillers or other modifiers etc, used during the manufacturing processes and use of epoxy resins. The physical state may vary from vapour to liquid to semi-solid or solids, depending on their viscosity, method of preparation and use.

Epoxy resin systems have been used in a variety of applications including construction and building, automotive, aerospace, medical, electronics, offshore and engineering. Although considerable information is available in the literature on epoxy resin sensitisation, little is known about how to prevent or reduce the harmful effects in industrial applications such as building and construction. HSE has been concerned about epoxy skin sensitisation problems, particularly in the construction industry where use of protective clothing (e.g. gloves) or environment (e.g. clean room) is less common or practical. HSE, therefore, commissioned TWI to undertake a project to study skin sensitisation effects of epoxy resins, particularly when used in the construction industry. This project is expected to be in three phases:

Phase 1 - Technical appraisal
Phase 2 - Experimental trials
Phase 3 - Technology transfer to industry.

The results of the technical appraisal are described in this report.

2. OBJECTIVES

The two main objectives of this work (Phase 1) were:

1) To carry out a literature survey and review selected papers on epoxy skin sensitisation, particularly for the construction industry.

2) To carry out an industrial survey contacting major suppliers, and users of epoxy resins in the construction industry to identify current information and problems associated with epoxy resin sensitisation.

3. APPROACH

The project was undertaken in three parts:

Part 1 - Press release
Part 2 - Literature survey
Part 3 - Industrial survey.

4. PRESS RELEASE

A press statement describing the objectives of this project was prepared in agreement with the HSE and released to a number of journals and magazines.

5. LITERATURE SURVEY

5.1. APPROACH

A comprehensive literature survey was carried out to identify the relevant published information.

A number of literature searches were performed on this topic. Four searches were performed as follows:

1. An overall search on dermatitis, eczema, skin sensitisation/photosensitisation or allergies and epoxy resins was performed on the Medicine and Toxicology groups of databases on the DIALOG host.

   The databases searched were:

   Biosis Previews; SciSearch; Dissertation Abstracts Online; SPORTDiscus; Inside Conferences; ELSEVIER BIOBASE; EMBASE; Conference Papers Index; MANTIS; JICST-EPlus; General Sci Abs/Full-Text; TGG Health & Wellness DB; HealthSTAR; MEDLINE; Toxline; Aidsline; Cancerlit; CAB HEALTH; Allied & Alternative Medicine(AMED); EMBASE Alert; FEDRIP; Science; SciSearch; AMA Journals; New England Journal of Med.; The Lancet; ExtraMED; NTIS; Meteor & Geoastro.Abs.; Enviroline; Pollution Abs; CAB Abstracts; Food Sci.&Tech.Abs; FOODLINE(R): Food Science & Technology; FOODLINE(R): Current Food Legislation; Env.Bib.; SEDBASE; Int.Pharm.Abs.; Life Sciences Collection; Wilson Appl. Sci & Tech Abs; Energy SciTec; WasteInfo; Occ.Saf.& Hth.; Pharm-line; Drug Info.; Pesticide Fact File; DOSE; Chemical Safety NewsBase; Material Safety Data Sheets; Material Safety Summary Sheets; RTECS; CHEMTOX; CA SEARCH; Adis Newsletters(Current); Adis Newsletters(Archive);

   416 items were identified for initial scrutiny.

2. A search on the safety of the use of epoxy resins in the construction industry and civil engineering was performed on the Safety group of databases on the DIALOG host.

   The databases searched were:

   Biosis Previews; NTIS; Meteor.& Geoastro.Abs.; SciSearch; Enviroline; Pollution Abs; CAB Abstracts; Food Sci.&Tech.Abs; FOODLINE(R): Food Science & Technology; FOODLINE(R): Current Food Legislation; Inside Conferences; Env.Bib.; SEDBASE; EMBASE; Int.Pharm.Abs.; Life Sciences Collection; JICST-EPlus; Wilson Appl. Sci&Tech Abs; Energy SciTec; WasteInfo; MEDLINE; Toxline; Occ.Saf.& Hth.; CAB HEALTH; EMBASE Alert; Pharm-line; Drug Info.; Pesticide Fact File; DOSE; Chemical Safety NewsBase; Material Safety Data Sheets; Material Safety Summary Sheets; RTECS; CHEMTOX; CA SEARCH; Adis Newsletters(Current); Adis Newsletters(Archive); SciSearch; AMA Journals; New England Journal of Med.; The Lancet; USP DI(R).

3. A search for review papers on the use of epoxy resins in the construction industry and civil engineering was performed on the Engineering and Materials groups of databases on the Dialog host.

   The databases searched were:

   INSPEC; NTIS; Ei Compendex; Mechanical Engineering Abs; World Surface Coatings Abs; METADEX; Aluminium Ind Abs; SciSearch; Dissertation Abstracts Online; Transport Res; Global Mobility Database; Inside Conferences; TULSA (Petroleum Abs); JICST-EPlus; FLUIDEX; Wilson Appl. Sci & Tech Abs; Energy SciTec; Aerospace Database; ICONDA-Intl Construction; Abs. in New Tech & Eng.; Mathsci; PAPERCHEM; PIRA; Eng Materials Abs; ChemEng & Biotec Abs; RAPRA Rubber & Plastics; Ceramic Abstracts; SciSearch; World Textiles; AESIS; Textile Technol.Dig.; Packaging Sci&Tech; Science; CA SEARCH.

   17 items were identified for initial scrutiny.

4. A search for epoxy resins and dermatitis or skin sensitisation in the construction industry or civil engineering was performed on the Medicine, Toxicology and Safety groups of databases on the Dialog host (as listed above).

   12 items were selected and printed in full.

   In each case searches were restricted to papers in English published in the last 15 years. For searches 1 and 2, an initial list of titles and indexing terms was printed for scanning and selection of items of interest. Bibliographic references, abstracts and keywords were printed for the selected records for further evaluation and selection of papers to obtain.

The literature covered a wide range of relevant topics including epoxy types, skin sensitisation reports, preventative measures etc.

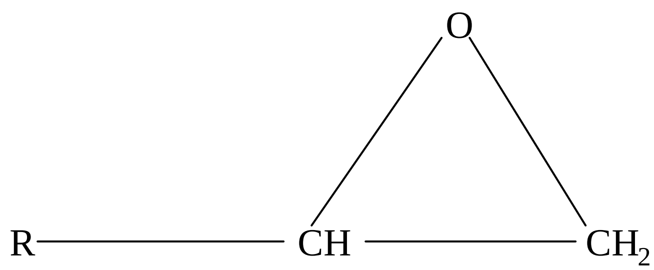
A review of the selected papers is provided in the following section.

5.2. BACKGROUND TO EPOXY RESINS

5.2.1. General

Epoxy resins [1] have been the subject of numerous patents, papers and other publications since their significant commercial debut around 1947. This extensive interest in epoxy resins originated from the extremely wide variety of chemical reactions and materials that can be used for the curing and the many different properties that result. The chemistry is unique among the thermosetting polymers. Unlike formaldehyde resins, no volatiles are given off during the cure. The type of chemistry involved in hardening the epoxy resins permits the user to cure over a wide range of temperatures (e.g. 3°C in seawater to 200°C [snap epoxy adhesives in electronic applications]). Depending on the chemical structure of the curing agent and the curing conditions, it is possible to obtain toughness, chemical resistance, mechanical properties ranging from extreme flexibility to high strength and hardness, high adhesive strength, good heat resistance and high electrical resistance. The uncured resins may have a variety of physical forms ranging from low viscosity liquids to tack-free solids. As a result of this versatility, these products have found use in protective coatings, adhesives, body solders and caulking compounds, binders, inks, tooling compounds for moulds, sealants and encapsulant, textiles and fibre reinforced polymers.

The term epoxy is a prefix referring to a bridge consisting of an oxygen atom bonded to other atoms already united in some way. The epoxide group is a three membered carbon, carbon, oxygen ring structure which is also known as oxirane group: (I).



(I)

The epoxy resin may contain one or more oxirane groups, usually when R = $-CH_2$.

The ability of this group to undergo a large variety of polymerisation and crosslinking reactions leads to many different types of epoxy resins with a wide range of commercial and physical properties.

The epoxy resin system usually consists of the following constituents:

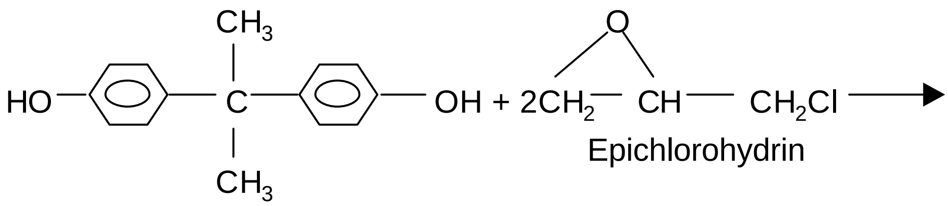
(i) Base resin
(ii) Curing agents
(iii) Reactive diluents
(iv) Solvents
(v) Plasticisers, flexibilisers and toughening agents
(vi) Fillers including pigments and reinforcing fibres.

Skin sensitisation may be caused due to the base resin (e.g. diglycidyl ether of bisphenol A (DGEBA, IV)) or other constituents (e.g. curing agents, diluents etc). A review of the main constituents of epoxy resin compounds and their contribution to skin sensitisation will be given in the following sections.

5.3. MAIN CONSTITUENTS OF EPOXY SYSTEMS AND THEIR CONTRIBUTION TO SKIN SENSITISATION

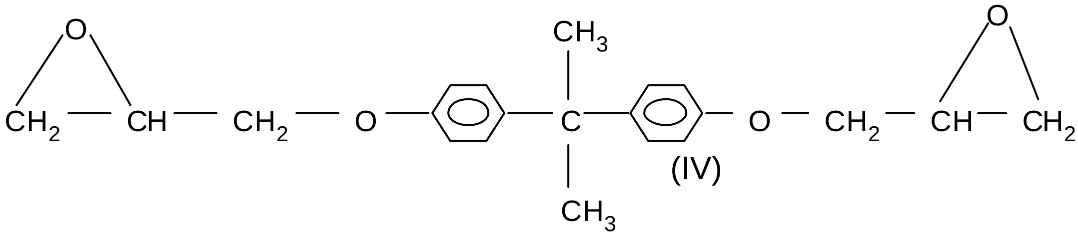
5.3.1. Main Type of Base Epoxy Resin

About 90% of most of the different epoxy resins are made using DGEBA as the base resin. The DGEBA is formed as a result of reaction between bisphenol A (II) and epichlorodydrin (1-chloro-2,3-epoxy propane; δ-chloropropylene oxide) (III):

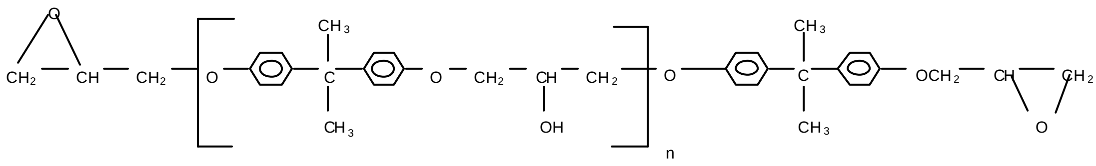


Bisphenol A

(II) (III)



Higher molecular weight epoxy resin based on DGEBA will have the following chemical structure:



IV = diglycidyl ether of bisphenol A

MW	n
340	0 - liquid
624	1 - liquid
908	2 - solid
1192	3 - solid

When n = 0, a low molecular weight product, which is the major component of commercial low molecular weight epoxy resin is produced (DGEBA) [2]. Low molecular weight epoxy resin has an average molecular weight below 1000, with a high amount of MW340 oligomer. Fregert and co-workers [2] reported that it is mainly the epoxy resin oligomer of MW340 which is responsible for epoxy resin allergy.

5.3.2. Sensitisation Effects due to Base Epoxy Resins

5.3.2.1. Epichlorohydrin and bisphenol A

Sensitisation due to epichlorohydrin (ECH) and bisphenol A have been reported by a number of workers [3-5].

Sensitisation to ECH was reported in six patients with occupational contact allergy [6]. In two cases, an isolated positive test to ECH was found. In the remaining four cases, concomitant positive reactions were seen to epoxy resin (DGEBA epoxy resin with an average molecular weight (MW) of 385) and to liquid epoxy resin (MW = 370).

The data presented in this work indicated that in the majority of cases, primary sensitisation to ECH occurred in epoxy resin plants. Although bisphenol A based epoxy resins can be manufactured by the reaction of bisphenol A and ECH in a closed manufacturing system, accidental leakage, maintenance duties or contamination of equipment can expose individual workers to ECH. It was suggested that adequate preventative measures to avoid skin-contact with ECH should be used to prevent ECH sensitisation. Allergy to bisphenol A was not found in patients in this case. However, contact dermatitis due to bisphenol A was reported by other workers [7-8]. It was reported [7] that a man who worked with liquid waxes for the previous five years, developed an acute dermatitis of his right hand. The dermatitis first appeared six months earlier, and on three occasions rapidly settled when he was off work, only to relapse on his returning to work. He did not wear gloves at work and was not exposed to irritant chemicals.

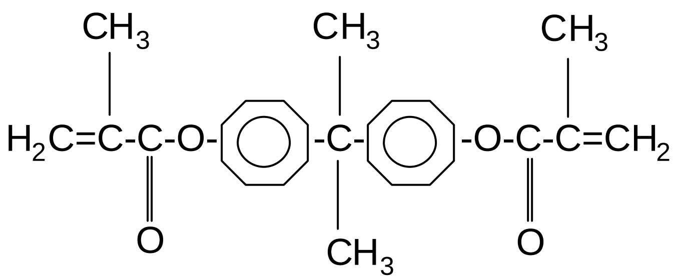
In general, as Jolanki [9] pointed out, occupational contact dermatitis due to ECH and bisphenol A is uncommon. In the finished DGEBA epoxy resin, the proportion of free ECH is less than 0.001%. The proportion of bisphenol A is even smaller because, in the manufacturing process ECH is always in excess to ensure completion of reactions. Reports of bisphenol A sensitisation are rather controversial [5]. Van Joost et al [5,6] found very few cases of bisphenol A allergy in workers at epoxy resin plants.

5.3.2.2. Non-diglycidyl ether of bisphenol A

Most people who experienced contact allergy have been sensitised to DGEBA type of epoxy resins [9]. Since the 1980s allergic contact dermatitis has also been reported from non-DGEBA epoxy resins [10-12]. In addition cycloaliphatic and brominated type of epoxy resins have also been found to be causes of allergic contact dermatitis (ACD) [12-14]. Many patients sensitised to non-DGEBA epoxy resins did not have contact allergy to DGEBA epoxy resins.

5.3.2.3. Epoxy acrylates

Epoxy acrylates (V), also called vinyl esters, are produced from epoxy resins and methacrylic acids or bisphenol A and glycidyl methacrylate.



2,2-bis (4-(methacryloxy)phenyl)) propane (V)

Epoxy acrylates are used in dental filling and coating materials as well as other applications (e.g. printing inks). Epoxy acrylate can be cured using peroxides and tertiary amines, by visible or ultraviolet light. Epoxy acrylates are weak to extreme sensitisers [9].

Despite the increasing use of epoxy acrylates in dental and industrial applications relatively few reports of contact allergy due to these compounds have been reported [10,15-17]. The sensitised subjects have mainly been workers in the UV-light printing industry [15] or in dental nursing [16] and UV curable epoxy paints [17].

5.3.3. Curing Agents

5.3.3.1. Types

Epoxy resins curing agents can be divided into three technologically important classes [18]:

(i) active hydrogen compounds, which cure by polyaddition reactions

(ii) ionic initiators, which are sub-divided into anionic and cationic

(iii) crosslinkers, which couple through the hydroxyl functionality of higher-molecular-weight bisphenol A type epoxy resins.

The chemistry of the first class of curing agents currently used with epoxy resins is based on polyaddition reactions that result in coupling as well as crosslinking. The most widely used of these are based on active-hydrogen compounds (polyamines, polyacids, polymercaptans, polyphenols etc), undergo polyadditions via the compound containing the active hydrogen and the terminal carbon of the epoxide group.

Tertiary amines are the general class of anionic initiators most accepted commercially as curing agents for epoxy resins. Pyridine, 2,4,6–tris (dimethylaminomethyl)phenol (tris-DMP), benzyldimethylamine and triethylamine are typical examples of tertiary amines.

A wide variety of compounds – notably the halides of tin, aluminium, zinc, boron, silicon and iron, as well as fluoroborates of many of these metals – are cationic initiators for epoxy resins. Typical example of this type of initiators are BF_3-amine or BF_3-ether complexes.

Among active-hydrogen compounds dicyandiamide is one of the most widely used latent curing agents for epoxy resins. This curing agent has found extensive use in three main epoxy technologies:

a) epoxy powder coating
b) epoxy composites and reinforced laminates for the electrical industry
c) one-component adhesive formulations.

The latent nature of dicyandiamide depends on the fact that it is insoluble in the epoxy resin at ambient temperatures.

A comprehensive list of some of the most commonly used curing agents in epoxy resin formulations is given in a recent publication by Jolanki [10]. In epoxy resins used as in two-part systems, the curing agents are added to the resins immediately before the application, and the subsequent crosslinking occurs at either an ambient or an elevated temperature. Aliphatic and cycloaliphatic polyamides are low-viscosity liquids which react readily with epoxy resins at ambient temperatures. Aromatic polyamides require an elevated curing temperature.

5.3.3.2. Sensitisation effects

Polyamines have irritating and sensitising effects to the skin and respiratory tract. To overcome these disadvantages, polyamides and epoxy-amine adducts that are less volatile, reactive, sensitising and irritating have been developed.

The sensitisation caused by epoxy resin hardeners has been reported by a number of investigators [10,19-24]. Polyamine hardeners have been found to be contact irritants and sensitisers as early as in 1951 [19]. Kanerva and co-workers [20-21] described ACD caused by a number of epoxy hardeners including polyamines. It was shown that a woman patient developed dermatitis from a two-compound epoxy spray paint system. Patch testing with epoxy resin was negative, but tris-DMP, used in the paint hardener, induced an allergic patch test reaction. The woman patient developed dermatitis on the face, neck, upper thorax and arms. Her dermatitis cleared on sick leave, but the symptoms reappeared within a day when she returned to work, even when she did not paint, but worked in the facilities where painting was done, suggesting that part of her symptoms were due to airborne substances.

In an earlier study Kanerva [21] and co-workers evaluated 113 patients with occupational ACD from epoxy resin compounds during 1974-1990. They showed that 30 of these patients had occupational ACD from epoxy hardeners. The cases of five patients were studied in more detail. One patient had contact allergy to diethylenetriamine (hardener of a spray paint) and another from that of a mortar adhesive. Two patients, a painter and a process worker, had become allergic to tris-DMP [21-22] and to the isophoronediamine (IPDA) in the hardeners of epoxy paints and coatings that they handled. The fifth patient had become sensitised to three components of the hardeners (i.e. to IPDA, trimethylhexamethylenediamine and xylylenediamine) of a two-part epoxy resin used for concrete floor coatings .

Other types of epoxy hardeners are the phthalic anhydrides, such as methylhexahydrophthalic anhydride (MHHPA) and methyltetrahydrophthalic anhydride (MTHPA). Kanerva and co-workers [23] showed that exposure to MHHPA can cause ACD as well as allergic rhinitis and an immediate contact skin reaction.

ACD from epoxy resin hardeners during the manufacture of thermosetting coating paints was reported by Foulds and Koh [24]. Five production operators from two factories manufacturing thermosetting coating paint developed work-related skin disorders within 12 months of the introduction of a new powdered paint product. All such workers were found to have ACD from two epoxy resin hardeners, both of which were commercial preparations of triglycidyl isocyanurate (TGIC). Two of the workers had concomitant sensitisation to epoxy resins in the standard series and several of the epoxy resin preparations at the workplace. TGIC had been reported as a contact sensitiser both in persons producing the chemical and among end-users of TGIC containing products.

5.3.4. Reactive Diluents

5.3.4.1. Types

Because epoxy resins are sometimes too viscous for use in certain applications, the viscosity is often reduced by the addition of solvents, plasticisers, modifying resins and reactive diluents [10 and 18]. The reactive diluents are normally glycidyl ethers and sometimes, glycidyl esters. They may have aliphatic or aromatic structures and contain epoxy group in their molecule [10]. Low-viscosity epoxy compounds (e.g. 1,4-butanediol digylcidyl ether) are normally used as diluents. The type and amount of diluent will affect viscosity and curing characteristics of epoxy systems. There are other diluents (e.g. tetrahydrofuran, lactone, unsaturated polyesters) which are non-epoxy compounds.

5.3.4.2. Sensitisation effects

Reactive diluents were also found to cause contact allergy [25-27]. Reactive diluents in epoxy systems have been reported as strong sensitisers in guinea pigs [25] and in humans [26]. Contact allergy to reactive diluents without contact allergy to epoxy resins is also possible [27]. These materials are more volatile than DGEBA epoxy resins, and may cause an airborne dermatitis pattern.

The sensitisation capacity of six epoxy reactive diluents in pigs was investigated by Thorgeirsson [25]. All the low molecular weight reactive diluents (MW = 175-360) proved to be sensitisers. One diluent of higher molecular weight (aliphatic polyglycidyl ether of MW = 1700) produced no reactions. Epoxy dodecane and the low molecular weight mono- and diglycidyl ethers were found to cause sensitisation. The glycidyl esters were as sensitising as the glycidyl ethers.

Most patients exposed to reactive diluents were reported to be sensitised and allergic to phenylglycidyl ether, cresylglycidyl ether, hexandiol diglycidyl ether, butandiol diglycidyl ether or butyl glycidyl ether [28]. Rare reactive diluent contact allergens are allyl glycidyl ether, neopentyl glycol diglyadyl ether [9-10].

5.4. SENSITISATION TO OTHER EPOXY COMPOUNDS

As mentioned earlier, TGIC can also cause an allergic response. This chemical is a known irritant [28-29] and has also been shown to be an allergen [29]. Operators may become sensitised to TGIC from short-term exposure to the chemical in the production of TGIC, in the manufacture and use of TGIC-containing polyester powder paints, and in the manufacture of circuit boards [29 and 30].

5.5. PHOTOSENSITIVITY TO EPOXY RESINS

Cases of photosensitivity and photodermatitis (light-responsive dermatitis) to epoxy resins were reported by Herbert and Kaidbey [31]; persistent photosensitivity developed in eight men following occupational exposure to hot epoxy resin fumes. The condition was limited to sites the resin contacted. Small doses of ultraviolet-A light (2-5 Joules/cm^2) evoked abnormal reactions consisting of erythema and papules in the clinically involved skin. Positive photopatch tests to epoxy resins were observed in four subjects, and to bisphenol A in all. It was concluded that the photosensitivity was probably related to bisphenol A or to a closely related chemical. Aromatic compounds such as bisphenol A are well-known UV absorbers.

5.6. FORMULATION AND USAGE

Firstly, it is worth mentioning that the use of epoxy resins has increased in recent years and is expected to be used more in the future. This is based on the growing acceptance of epoxy systems in a variety of different industrial applications as adhesives, coatings, fillers and epoxy grouts, etc. There are several factors which have contributed to the increased use of epoxy resin grouts in ceramic tiling over the last ten years [32], including:

1. Changes in the UK Food Hygiene Laws, as a result of EC Directives, which now stipulate the requirements for floor and wall surfaces in food preparation, processing and treatment areas. Joints between the tiles must be totally impervious, easy to clean and disinfect and should not taint food. Epoxy resin grouts fulfil these criteria.

2. In recent years several problems have arisen of grout erosion of cementitious grouts in swimming pools. As a result, leading architects have begun to favour the use of epoxy grouts, despite the increased cost. This has seen a rise in sales of epoxy grouts.

3. Also in swimming pools, the large number of leisure pools built over the last 10-15 years where features such as wave machine are incorporated, has seen epoxy grouts used in the beach areas, for abrasion resistance.

4. Over the last 10 years there is no doubt that epoxy formulations have become more user-friendly from an application point of view. Most modern epoxy grouts are water washable/wipable, which means that they are easy to apply

and clean off. Thus, there is not the same resistance from the tiling contractors to using epoxies.

5. The increased use of power showers in domestic shower cubicles has established the need for a tough waterproof grout to withstand these conditions, epoxies are normally specified in these locations.

6. Epoxy grouts continue to be specified for their chemical resistance and this sector of the market is as relevant today as it was 10 years ago.

In conclusion therefore, it can be seen that there has been a substantial increase in the specification and use of epoxy resin based grouts in the construction industry.

Furthermore, there has been an increasing tendency to use reactive diluents in epoxy resins. Benefits of using reactive diluents include improved wetting of pigments, application properties, toughness and flexibility. These materials have a higher vapour pressure than epoxy resins, and therefore can present an air-borne hazard as well as the ability to penetrate skin. As described in our report, epoxy resins with high amounts of epoxy oligomer (molecular weight (MW) = 340) is mainly responsible for epoxy resin sensitisation. The sensitising capacity of epoxy systems can be decreased in inverse proportion to the increase in the average MW of the resin mixtures. Although some efforts are being made to produce higher MW epoxy resin systems, in practice this is not always possible because of the effects on various properties of the resins.

Furthermore, as the demand for the development of a new generation of epoxy resins with improved properties increases, new hardeners, diluents or epoxy base resins may be introduced with unknown skin sensitisation effects.

A new survey was also carried out to identify current and future trends in the use of epoxy resins [57]. Table 1 represents a forecast of European market growth in structural adhesives by type and end-use during 1999-2004. The end use of epoxy paste and epoxy film is expected to grow by 1.5% and 4.5% per year respectively from 1999 to 2004. In terms of tonnage, 11645.4 epoxy paste is expected to be used by 2004 (Table 2) in comparison to 641.7 tonnes of epoxy film. The growth in the use of epoxies is considerably greater than other types of structural adhesives with the exception of polyurethane (26489.3 tonnes by 2004).

The forecast of European market growth in epoxy paste structural adhesives by country and end use during 1999-2004 are shown in Table 3. The UK and Ireland show higher total % growth/year (1.7%) compared to the European growth average (1.5%).

The forecast for use of epoxies in industrial flooring for the next four years by type and price is shown in Table 4. In this case use of epoxy resins are expected to grow steadily from £16.3 million in year 2000 to £22.3 million in year 2004. This is higher than polyurethanes (from £10.9 million to £15.1 million).

Table 5 summarises the forecast for the UK market for industrial flooring in terms of prices and % change from 2000-2004 [58]. Considerable growth (+23%) is expected for the industrial flooring market in 2002.

5.7. CLINICAL INVESTIGATION OF EPOXY DERMATITIS

A number of publications have been devoted to the analysis of long-term (5-10 years) data on epoxy dermatitis in a large number of patients [9,33-36].

Jolanki [9] reported that of 3,713 patients examined at the Institute of Occupational Health, Helsinki during 1974-1990 for suspected occupational skin disease, 1,832 patients (49.3%) received a primary diagnosis of occupational skin disease and 1,881 (50.7%) were considered cases of non-occupational skin disease. Of all the occupational skin diseases, 901 (49.2%) cases were ACD, 843 (46.0%) were irritant contact dermatitis, 36 (2.0%) were contact urticaria and 52 (2.8%) were classified as "other".

One hundred and thirty patients were diagnosed in 1974-1990 at the institute as having occupational skin disease due to occupational exposure to epoxy compounds. Epoxy resin compounds, epoxy acrylates and other epoxy compounds were involved for 120, 6 and 4 of the patients, respectively.

Among 1,844 patients with occupational skin diseases diagnosed in 1974-1990, 142 patients (7.7%; 92 men and 50 women) were considered to have skin disorders from current occupational exposure to epoxy compounds. In a total of 135 cases the diagnosis was ACD. Of the 142 dermatoses caused by occupational exposure to epoxy compounds, 132 cases (93%) were due to epoxy resin compounds (i.e. epoxy resins, reactive diluents and hardeners). Six were due to epoxy acrylates (or bisphenol A in epoxy acrylates) and four due to other epoxy compounds.

Kanerva, Jolanki and co-workers also published the results of clinical trials between 1974-1988 in other reports [33]. An analysis of 10 years (1974-1983) of statistics was carried out at the Institute of Occupational Health Helsinki, Section of Dermatology, which is devoted to occupational dermatology. A total of 1,082 cases of occupational skin diseases were diagnosed during this period. Allergic (50.1%) and toxic eczema (47.1%) comprised the majority of occupational cases of dermatitis. The most frequent cause of allergic occupational eczemas were rubber chemicals (19.9%), chromates (18.8%) and epoxy resins (13.1%).

In a separate study, Jolanki and co-workers [34-35] published the results of five years work on occupational skin disease due to epoxy compounds. 891 patients suspected of having an occupational skin disease were investigated during 1984-88; 540 cases (60.6%) proved to be occupational diseases and 351 (39.4%) non-occupational. Allergic (264 cases, 48.9%) and irritant (238 cases, 44.1%) contact dermatitis comprised the majority of occupational skin diseases. This study comprised 40 patients who had acquired skin disorders from present or past occupational exposure to epoxy resin compounds.

Nixon and Frowen [36] described the result of a study of occupational skin disease amongst workers exposed to epoxy resins in Australia. Among 234 studied, 25 workers were found to have allergic reactions to epoxy chemicals. The majority of workers with allergic reactions to epoxy chemicals did not take time off work, and almost 30% of workers with allergic reactions to epoxy chemicals did not even consult a doctor.

Unpublished data from the EPIDERM and CPRA reporting schemes for 1993-1999 were reviewed [37] suggesting that workers in the construction industry had suffered from a substantial number of epoxy resin disorders.

5.8. EPOXY RESIN IN THE CONSTRUCTION INDUSTRY

5.8.1. Uses of Epoxy Resins

In the building and construction industry, epoxy resins are used for a variety of applications such as:

- coating and paints
- impregnating and repairing concrete, brick and wooden structures
- repair and sealing of pipeworks, window frames etc
- adhesives for ceramic tiles
- binders and resins for fibre reinforced composites.

5.8.2. Epoxy Resins Skin Sensitisation in the Construction Industry

The epoxy resins commonly used in the construction industry are of low molecular weight, and therefore have a higher sensitising potential compared with oligomers of higher molecular weight [38].

Occupational contact dermatitis due to epoxy resin in a fibreglass binder was reported by Holness and co-workers [39]. They have shown that eight workers handling fibreglass coated with uncured epoxy resin, out of a population of approximately 130 workers, developed dermatitis of their hands and forearms. Four also had involvement of the head and neck. Patch testing showed the presence of contact allergy to epoxy resin in six cases and one worker had continuous sensitivity to cresyl glycidyl ether. Workers handling the coated epoxy material after it had been heat-cured were not affected, even if they had had problems with dermatitis whilst handling the uncured coated fibre. Recommendations were made to management with regard to the use of personal protective equipment to improve cutaneous hygiene and reduce the possibility of induction of contact allergy.

Van Putten and co-workers [40] reported cases of hand dermatoses and contact allergic reactions in construction workers exposed to epoxy resins. In 23/135 (18%) of workers exposed to epoxy resins, work-related dermatoses on the hands and/or forearms had been present. In all workers, patch tests were performed with epoxy resin, IPDA, triethylenetetramine and xylenediamine. Positive patch tests were observed in 27 of the 135 exposed workers (20%), 13 of whom had never previously experienced skin problems. Epoxy resins accounted for the majority of positive reactions – only half of all workers had received safety instructions. The wearing of gloves (mostly cotton), intended to protect the skin had an adverse effect. This study was aimed at persons preparing and using epoxy resins for coating, flooring, impregnating and repairing concrete, brick and wooden structures. Housepainters were excluded. Mixing and application of epoxy resins in the construction industry is, in practice, mostly done by hand and on the spot, using simple methods. Contamination of the workers' skin occurs easily. Thus, the development of a contact allergy followed by an eczematous eruption may be expected, although in this study not all persons with positive patch tests had experienced eczema. It was concluded that among various materials tested epoxy resin was clearly the offender, the curing agent played an additional role in this respect. These researchers suggested the following protective measures to reduce skin sensitisation effects:

(i) more regular and frequent use of better protective clothing
(ii) use of solvents especially developed to clean the skin and the tools of sticky remnants of the substances to reduce skin sensitisation in these cases.

Finally, it was suggested that better instruction of the workers on the potential dangers of epoxy resins should be mandatory.

In a separate report Goh and co-workers [41] described occupational dermatitis in a prefabrication construction factory. 272 workers were interviewed, examined and patch tests exposed to a number of materials including rubber mixes and epoxy resins. 2.5% (1/38) of the patients were allergic to rubber chemicals in gloves, 57.9% (22/38) had irritant contact dermatitis to cement. One worker had asymptomatic epoxy resin sensitivity.

Cement and epoxy dermatitis in underground workers during construction of the Channel Tunnel were also the subject of a study by Irvine and co-workers [42]. The construction of the Channel Tunnel was one of the largest civil engineering projects ever undertaken. The British contribution employed 5,900 underground workers, and a number developed dermatitis during 1990-1991. As a result, the Translink Joint Venture Medical Centre set up a surveillance programme aiming to monitor and investigate the men working closely with cement as well as other groups of workers with skin problems. Men attended the Medical Centre voluntarily and were assessed, including history, examination and patch tests to a series of 15 test substances (from the European Standard Series). 1,138 men were seen at the Medical Centre regarding their skin and 332 were diagnosed as having occupational dermatitis, past or present. Allergy to epoxy resin was found in 25 out of 86 grouters who were patch tested. Part of the work of the grouters involved the repair of cracked concrete segments from the remedial gantries and back-grouting platforms of tunnel boring machines, and various epoxy cements were used for this purpose. Only three men had to change their occupations because of their skin disease. Most cases of occupational dermatitis improved with regular medical supervision, education and personal protective measures, with relocation to less exposed work where necessary. Many cases cleared as the tunnel entered better terrain.

Sensitisation to epoxy resin systems in special flooring workers was described by Conde-Salazar and co-workers [43]. Floor covering which will be exposed to aggressive agents, continual friction or percussion contains epoxy resins and derivatives. The laying of resin-based flooring is done by applying paints, liquid pastes or mortars containing epoxy resins to the surface to be treated. They are spread with rakes, brushes etc until reaching the desired thickness, which usually varies between 0.5-15mm. Fifteen male construction workers who specialised in the application of special floorings were studied. The epoxy resin used in this case contained bisphenol A with an average molecular weight of 700-950. Fourteen of the 15 patients patch tested showed sensitivity to epoxy resin.

In a follow on study, Conde-Salazar and co-workers [44] reported the patch test results of 449 construction workers who went as patients to a Dermatology Clinic in Spain during 1989-1993. 65.5% (268) out of those patch tested showed one or more reactions connected with their work. Chromate at 42.1% was the main allergen, followed by cobalt, 20.5%, nickel 10% and epoxy resin 7.5% (31 cases). 106 (25.9%) of patients showed sensitisation to rubber compounds.

A comparative study of contact allergies among construction and non-construction workers attending contact dermatitis clinics in Germany between 1989-1993 was described by Geier and Schnuch [45]. 205 patients working in the construction industry were patch tested. The result of this study was compared with those of 5,706 men tested during the same period who did not work in the building industry. The five most frequent allergens among the patients working in the construction industry were potassium dichromate (31.9%), cobalt chloride or sulphate (15.0%), nickel sulphate (8.3%), thiuram mix (7.8%) and p-phenylenediamine (7.7%) and epoxy resins (4.7%). Differences in sensitisation frequency between both groups were significant for potassium dichromate (31.9% versus 7.1%), cobalt salts (15.0% versus 4.9%), thiuram mix (7.8% versus 3.0%) and epoxy (4.7% versus 1.8%).

Contact allergies to thiurams are often observed in the building trade. One source of exposure to thiurams and other rubber ingredients in the construction industry is the use of rubber gloves and, in some cases, of rubber masks as well as the handling of window isolations, seals or rubber handles of tools as, for example, hammers.

Occupational sensitisation to epoxy resin and reactive diluents in marble workers was investigated by Angelini and co-workers [46]. Ten out of 22 marble workers handling a bicomponent resin, based on epoxy resin and ortho-cresylglycidyl ether (CGE), developed contact dermatitis and airborne contact dermatitis 20 days to 2 months after exposure. All 22 subjects were patch tested with epoxy resin, bisphenol A, ECH and a series of reactive diluents. The 10 symptomatic subjects were all positive to the reactive diluent CGE and four of them also to epoxy resin. The other reactive diluents that gave positive reactions were phenylglycidyl ether (7 cases) cyclohexanedimethanol glycidyl ether (2 cases), 1,6-hexanediol diglycidyl ether (2 cases) and ullyl glycidyl ether (1 case). The findings of this study suggested that allergic potential was directly proportional to the electronic charge available, for all electron-rich chemicals (on solvent, reagents, polymers etc) that interact with the glycidyl ether group. Lesser, but still noticeable, effects were detected when activation of the glycidyl group was related to the possible formation of intramolecular hydrogen bonds. In practice, the occupational problem was partly solved by changing the type of glycidyl ether.

This study showed a very high percentage of sensitisation to CGE (MW = 164) affecting 45% of exposed workers. This substance caused ACD by a dual route:

(i) a direct route which explained the hand dermatitis
(ii) an airborne route which explained the frequent localisation of dermatitis on the eyelids and other sites exposed to the vapour of the resin.

The latter route is favoured by the high vapour pressure of CGE, far higher than that of epoxy resin, and by resin being applied manually on hot marble slabs, therefore, accelerating solvent evaporation. No allergic reactions to bisphenol A or ECH were elicited in this study.

Goh [47] reviewed the common industrial processes and occupational irritants and allergens in the construction, electronics and metal industries. The most common contact allergens in the construction industry included chromate, cobalt and nickel, rubber chemicals and epoxy resins. Rubber chemical allergy in construction workers is not uncommon. Many construction workers wear rubber gloves and boots only after developing cement dermatitis. They become more prone to sensitisation to rubber chemicals in their protective gear. Epoxy-containing cement, because of its special properties, has been used in special construction processes. Epoxy cement is used in lining underground tunnels where it offers waterproof lining. It is also employed as a grouting cement and as a filler. ACD from epoxy resins among construction workers is expected to increase as more repair, maintenance and tunnelling work is being carried out.

It was reported that a number of workers experienced minor, and one severe, rash using an epoxy mortar during resurfacing of the raisable section of Tower Bridge [48]. Two men were patch tested, both were positive to epoxy resins and to the epoxy resin that was supplied from the site. One of the users was also positive to the epoxy hardener.

The road surface over the section of Tower Bridge that raises and lowers has to be both light and durable. In the past this was done by embedding wood blocks in bitumen but these blocks had been there since 1962 and were becoming worn. A replacement surface had therefore been devised consisting of 2½" thick plywood panels surfaced with a tile (a composition product) and over the surface of this a bauxite grit embedded in epoxy mortar. Each ply panel was then embedded in a layer of epoxy mortar which was applied to a polyurethane base which had already been laid beneath the wood blocks.

The epoxy mortar consisted of three components:

- resin
- hardener
- sand.

After the resin and hardener were mixed together the sand was added and the material was then ready for laying on the polyurethane surface.

As a result of this work it was reported that one of the workers who was patch tested was allergic to the epoxy resin and he was positive to trimethylhexamethylenediamine. This was one of the components of the epoxy hardener which was used in the Tower Bridge work.

5.9. PREVENTION OF EPOXY DERMATITIS

Jolanki [10] reported that to prevent epoxy dermatitis complete avoidance of contact with causative allergens is always necessary. In a patient highly sensitive to epoxy compounds, even a minimal amount of an allergen may be enough to evoke the symptoms on the exposed skin. Most patients who have acquired occupational epoxy dermatitis have to quit their work. Quitting may also be beneficial for the prevention of possible respiratory allergy following the skin sensitisation. Jolanki [10] also suggested the following points for reducing or preventing epoxy sensitisation:

(i) Workers using epoxy compounds should be made aware of the risk of sensitisation.

(ii) Gloves made of laminated, multi-layered plastic (4H-glove, layers of polyethylene bonded to an inner layer of a copolymer of ethylene and vinyl alcohol) should be used.

(iii) Use of many types of gloves can reduce exposure to epoxy compounds and risk of sensitisation.

(iv) Unhealthy skin, including even small wounds and abrasions, should be protected from epoxy-compound exposure because of increased skin penetration

(v) The use of higher molecular weight epoxies may reduce the possibility of developing allergy.

Allergic contact dermatitis and prevention measures in the building and construction industry in Australia were described by Holmes [49]. Nineteen workplaces in the industrial coating sector of the building and construction industry were surveyed for implementation of safe work practices in the use of epoxy coatings. The survey identified 36 epoxy coating products in use, and found that instruction of workers in preventive measures was inadequate. The use of personal protection was also poor and the availability of material safety data sheets was low. It was recommended that safe work procedures should be incorporated into a negotiated industry code of practice for the prevention of epoxy resin ACD. This study also identified the failure of painting contractors, as distinct from major building and construction companies, in meeting basic provisions for contact dermatitis prevention.

Penetration of epoxy resin into a protective glove (light disposable polyethylene gloves and rubber gloves) was the subject of a study by Pegum [50]. He described how a gas pipe jointer using a mixture of an epoxy and a hardener developed dermatitis from epoxy resin of bisphenol A type. This substance penetrated plastic and rubber gloves. The worker was compelled to change his job. Pegum concluded that there was a need for a new type of glove which was impermeable to epoxy resin.

The use of protective gloves for epoxy resin systems were also described in a number of other publications [51-53]. The results of a recent study on the use of protective gloves for handling epoxy resins was reported by the Epoxy Resins Committee of the Association of Plastics Manufacturers in Europe (APME) in 1996 [51]. APME is the professional representative body for the European polymer producers and has over 40 members representing more than 90% of the Western Europe manufacturing capability. A working group consisting of members of the German professional trade association of the construction industry, together with representatives of other German trade associations (civil engineering and adhesive sectors) was constituted with the aim of developing a Safety Guide on the use of epoxy resins in the civil engineering area. This project related to problems of skin irritation and sensitisation potential of workers exposed to epoxy resin systems. In this study the resistance to permeation of and resistance to swelling of a number of epoxy resins and curing agents with different types of glove were investigated. The epoxy resins and curing agents were of similar formulations to those used in the construction/civil engineering industries as shown in Table 6. The properties of the selected gloves are shown in Table 7. The result of this study is presented in Table 8. The main conclusions derived from this study were as follows:

(i) Fluorinated rubber (FR) can be considered as a good material, suitable for all ten formulations tested. Drawbacks are its high price and its poor mechanical properties.

(ii) Butyl rubber and brominated butyl rubber (BR and BBR) are recommended for solvent-free formulations but cannot always be used with solvent-based products. A drawback is its price (higher compared to nitrile).

(iii) Polyvinyl chloride (PVC) can only be recommended for some solvent-free epoxy resins and epoxy curing agent systems.

(iv) Nitrile rubber (NBR) is suitable with some limitations. It has overall good properties, but should only be used for a short exposure time when handling solvent based formulations. Advantages of NBR are its low price and its excellent mechanical properties.

(v) Polychloroprene (CR) can only be used with few formulations and additional testing is required.

(vi) Natural rubber (NR) is not suitable for handling the tested epoxy resin or epoxy curing agent formulations.

Henriksen and Petersen [52] described development of a multi-layered, laminated glove (4-H), particularly suitable for safe handling of epoxy chemicals. It was shown that this glove was impervious to a number of chemicals, particularly epoxy resins for at least 4 hours at 21 and 35°C. The 4-H glove described in this work was very flexible and had a thickness of 0.07mm. It was suggested that during heavy manual work or the handling of sharp objects a thin latex or cotton glove should be worn under the 4-H glove to improve its puncturing and tearing strength. The cotton glove would be suitable to overcome perspiration problems The 4-H glove is also not intended for continuous or prolonged (>4 hours) use.

The suitability of the 4-H glove against penetration by epoxy compounds was also reported by Roed-Peterson [53]. Patients with a proven allergy to epoxy of the bisphenol A type or to methyl methacrylate monomer volunteered for this study. No positive reactions were seen in eight patients sensitive to epoxy resin or four patients sensitive to methyl methylacrylate.

Assessment of protective effects of a range of barrier creams and spray coatings against epoxy resins were reported [54-55]. Blanken and co-workers [54] studied the protective effects of barrier creams and spray coatings against epoxy resins. The protective capacity of four barrier creams and two methacrylate spray coatings against skin contact with epoxy resins were evaluated. The effects of these materials on the strength and on the surface area of patch test reactions caused by epoxy resin were assessed in 11 volunteers with a known allergy to epoxy resins. Standard amounts of barrier cream and spray coating were applied on the skin. Then patch tests were carried out with epoxy resin on the pretreated sites. After 24 hours patches were removed, 48 hours thereafter the strength and surface area of the reactions were scored. The use of two barrier creams (Kerodex and Dermotect) resulted in a significant reduction of the surface area of the patch test reactions. Spray coatings significantly reduced both the strength and the surface area of the reactions. The thickness of the applied barrier cream was reduced to 0.01mm (normally = 0.05mm) to shorten the experiment to 24 hours. The methacrylic sprays (originally developed for the protection of wounds) both showed protective properties. However, the applied protective layer remains sticky and, the coating is difficult to remove from the skin and may contain potential allergens. The development of other formulations without these disadvantages will be required. In general, the effectiveness and practical use of barrier creams and spray coatings in industrial use, particularly in the construction industry, have to be established.

The effects of both barrier cream and a polyethylene laminate glove (4-H) against epoxy resins were studied by McClain and Storrs [55]. Patch testing was used to evaluate the ability of a barrier cream (Stockogard with the active ingredient of a polyamine salt, Linoleic acid dimer) as well as the 4-H glove against allergic contact dermatitis to epoxy resin. This study showed this particular barrier cream can provide adequate protection against epoxy sensitisation. The 4-H glove promised protection against allergy to epoxy resin after 8 hours and a 48 hour exposure to the allergen.

6. INDUSTRIAL SURVEY

6.1. MATERIAL SUPPLIERS

Contact was made with a number of suppliers of epoxy resin systems. Many suppliers provided technical and safety data sheets about their products and expressed an interest to participate in any further experimental trials or technology transfer following on from this work. Most of the major suppliers referred to the report by APME's Epoxy Resin Committee [51], as described earlier in Section 5.9 with respect to epoxy resin sensitisation and to a safe handling guide to epoxy resins [56]. The guide [56] was developed by the Epoxy Resin Systems Task Group of the Society of the Plastics Industry Inc. Typical exposure effects associated with epoxy resin systems described in this guide are shown in Table 9. Exposure potential of production processes and tasks as well as chemical resistance of various gloves reported in this guide are reproduced in Tables 10 and 11. Table 11 shows that the best type of recommended gloves for epoxy resins is based on ethyl vinyl alcohol (4-H). Butyl rubber was the second best in terms of its effectiveness.

6.2. CONSTRUCTION INDUSTRY AND OTHER INSTITUTIONS

A press release was sent to a number of journals and magazines including those specifically devoted to the construction industry. Details about this project asking organisations and construction workers to contact TWI or HSE regarding skin sensitisation were published in the spring 2000 editions of Site Safe News and Building Worker Bulletin. A questionnaire (Appendix) was also sent to a number of construction companies. Ten responses were received. Seven companies stated that either themselves, or their contractors, used epoxy resins. Three companies reported skin sensitisation to the hands and lower arms of workers. One also described sensitisation to the neck, chest and other parts of the body as well as the arms. Very little detailed information was provided regarding the types of epoxy/curing agents involved, types of protective clothing used, or types of applications and environments where epoxies were handled. It is hoped to have further contact and follow on discussions with these organisations during later phases of this work.

7. SUMMARY AND CONCLUDING REMARKS

A comprehensive literature search was carried out to identify and review the most relevant publications related to epoxy resin sensitisation. An introduction is given to the basic chemistry and formulation of epoxy resin systems. Different types of base resins and reacting ingredients, including curing agents and diluents, and their contribution to epoxy resin systems sensitisation have been reviewed. A summary of the main findings is shown in the following sections.

7.1. EPOXY FORMULATION

It was shown that most people who experienced contact allergy have been sensitised to the DGEBA type of epoxy resin. However, ACD due to non-DGEBA epoxy resins has also been reported. Low molecular weight (MW) epoxy resin has an average molecular weight of <1000, with a high amount of MW = 340 oligomer. It was shown that it is mainly the epoxy resin oligomer of MW = 340 which is responsible for epoxy resin allergy. The low molecular weight resin sensitised all of the guinea pigs tested and can be classified as an extreme allergen. The sensitising capacity decreased in inverse proportion to the increase in the average MW of the resin mixtures.

Polyamine curing agents have been found to be contact irritants and sensitisers. Aliphatic and cycloaliphatic polyamines are low-viscosity hardeners which can melt with epoxy resins at room temperature. These curing agents may be employed in some two-part, room temperature curing epoxies used in the construction industry. Polyamides and epoxy-amine adducts that are less volatile, less reactive and less irritating have been developed to reduce skin sensitisation effects.

One-component epoxy systems contain curing agents which are inactive at storage temperature but initiate a curing process when heated. Typical latent curing agents include organic acid anhydrides. These types of curing agent may be used in one-part, powder epoxy or epoxy-polyester paints, one-part adhesive sealants or encapsulants and polymer composite laminates. Most of the publications referred to contact allergy to polyamine hardeners. A few reports on non-amine hardeners have been published.

Reactive diluents have also been found to cause contact allergy in both animals and humans. Contact allergy to reactive diluents without contact allergy to epoxy resins is also possible. These materials are more volatile than DGEBA epoxy resin and may cause an airborne dermatitis pattern. Again it was shown that low molecular weight (MW=175-360) diluents can cause sensitisation. A higher molecular weight diluent (aliphatic polyglycidyl ether) of MW = 1700 produced no reactions.

The use of epoxy resins has increased in recent years and they are expected to be used more in the future. This is based on the growing acceptance of epoxy systems in a variety of different industrial applications as adhesives, coatings, fillers and epoxy grouts, etc. There are several main factors which have contributed to the increased use of epoxy resin grouts in ceramic tiling over the last ten years, including:

As the demand for the development of a new generation of epoxy resins with improved properties increases, new hardeners, diluents or epoxy base resins may be introduced with unknown skin sensitisation effects.

7.2. PHOTOSENSITIVITY

Cases of photosensitivity and photodermatitis to epoxy resins were reported in workers exposed to hot epoxy resin fumes and small doses of UV light (2-5 Joules/cm^2). It was concluded that the photosensitivity was probably related to bisphenol A or to a closely related chemical. The epoxy resins commonly used in the construction industry are of low molecular weight, and therefore have a higher sensitising potential compared with oligomers or higher molecular weight materials. The presence of polyamine hardeners in two-part epoxy systems increases the possibility of dermatitis compared to acid anhydrides used in heat curing, one-part epoxies. Workers handling the coated epoxy fibreglass after it has been heat-cured were not affected.

7.3. MIXING AND APPLICATION

Mixing and application of epoxy resins in the construction industry is usually done by hand on site, using simple methods. Contamination of the workers' skin occurs easily. Therefore the development of a contact allergy followed by an eczematous eruption may be expected. It was also concluded among various materials tested, that epoxy resin was clearly the offender, and the curing agent played an additional part in this respect. Some construction workers may become allergic to rubber chemicals in gloves and this may sometimes be confused with epoxy resin sensitisation. Sensitisation to rubber chemicals in the construction industry may also occur as a result of exposure to thiurams and other rubber ingredients contained in rubber masks, rubber window isolation seals or rubber handles of tools (e.g. hammers).

7.4. USE OF EPOXY RESINS

The end use of epoxy paste and epoxy film is expected to grow by 1.5% and 4.5% per year from 1999 to 2004. In terms of tonnage 11645.4 epoxy paste is expected to be used by 2004 compared to 641.7 tonnes of epoxy film. The growth in the use of epoxies is considerably higher compared to other types of structural adhesives with the exception of polyurethane (26489.3 tonnes by 2004).

Epoxies in industrial flooring for the next four years by type were shown to grow steadily from £16.3 million in year 2000 to £22.3 million in year 2004. This is higher than polyurethanes (from £10.9 million to £15.1 million). Considerable growth (+23%) is expected for the industrial flooring market in the UK in 2002.

7.5. PREVENTION OF EPOXY DERMATITIS

For prevention of epoxy dermatitis complete avoidance of contact with causative allergens is always necessary. For reducing or preventing epoxy sensitisation, the following recommendations can be given on protective measures as a result of this project:

(i) Workers should be made aware of the risk of epoxy sensitisation.

(ii) Wearing of protective clothing, particularly effective gloves (e.g. fluorinated rubber gloves), should be mandatory. The protection should be regularly changed to ensure continuous effectiveness.

(iii) The use of higher (>900) molecular weight epoxy resins or diluents should be considered to reduce or prevent the possibility of developing an allergy.

(iv) Wherever possible, use of one-part, instead of two-part, epoxies can reduce the risk of skin contact during hand mixing.

(v) The use of two-part or pre-mixed epoxies supplied in single or twin cartridges, or mixing of two components with an automated internal mixer or dispensing equipment is highly advisable.

(vi) Contact with incompletely cured epoxy resins should be avoided.

(vii) Whenever possible, proper ventilation should be provided to avoid airborne dermatitis, where this is a problem.

(viii) Individuals with more susceptibility to dermatitis should not be selected to work with epoxies, to reduce risk of sensitisation.

(ix) Whenever possible, alternative epoxy systems with reduced risk of sensitisation should replace those causing harmful effects.

(x) Proper instructions should be given to workers regarding good housekeeping, education in hygiene, proper methods of disposal, handling procedures and remedies if skin sensitisation with epoxies is experienced.

(xi) The use of some barrier creams and spray coatings may be effective although their use in some applications, particularly in the construction industry, is often impractical.

(xii) All epoxy users should have access to material safety data sheets and clearly understand the possible harmful effects if not used properly.

(xiii) Damaged skins, including even small wounds and abrasions, should be protected from epoxy-compound exposure because of increased skin sensitisation.

It should also be noted that although laminated 4-H gloves have been found effective during exposure to epoxy resins, their use within the construction industry is considered impractical. This is due to their shape and lack of acceptable mechanical properties (tear and puncture resistance) for on-site use. Therefore, there is a need to develop gloves which are effective, practical and low cost for use with epoxy resins in the construction industry.

8. REFERENCES

1 May C A (Ed): Epoxy resins, chemistry and technology. * Second edition published by Marcel Dekker Inc, 1988.

2 Fregert S: 'Contact dermatitis from epoxy resin systems'. Occupational and Industrial Dermatology, 2nd Edition Year Book, Maibach H I (Ed), Chicago, 341-345.

3 Rycroft R J G, Menné T, and Frosch P J (Eds): 'Textbook of contact dermatitis'. Second revised and enlarged edition, published by Springer-Verglag, 1995, 550-554.

4 Cronin E (Ed): 'Contact dermatitis', Longman Group Ltd, 1980, Chapter 12, 595.

5 Van Joost T H, Roesyand I D and Satyawan I: 'Occupational sensitisation to epichorohydrin (ECH) and bisphenol A during the manufacture of epoxy resin'. *Contact Dermatitis* 1990 **22** 125-126.

6 Van Joost T H: 'Occupational sensitisation to epichlorohydrin and epoxy resin'. *Contact Dermatitis* 1988 **19** 278-280.

7 Freeman K and Warin A P: 'Contact dermatitis to bisphenol A in semi-synthetic waxes'. *Contact Dermatitis* 1984 **11** 259-261.

8 Srinivas C R, Devadiga R and Aroor A R: 'Footwear dermatitis due to bisphenol A'. *Contact Dermatitis* 1989 **20** 150-151.

9 Jolanki R: 'Occupational skin diseases from epoxy compounds'. *Acta Dermato-Venereologia Supplementum 159* 1991 **35** 159.

10 Jolanki R, Kanerva L and Estlander T: 'Epoxy resins'. Handbook of occupational dermatitis. Edited by Kanerva L, Elsner P, Wahlberg J E, Maibach H I. Springer Verlag, Heidelberg 2000, Chapter 73, in press.

11 Burrows D, Fregert S, Campbell H and Trulsson L: 'Contact dermatitis from epoxy resins tetraglycidyl-4,4'-methylene dianiline and o-diglycidyl phathalate in composite material'. *Contact Dermatitis* 1984 **11** 80-82.

12 Braze M, Edenholm M, Engström K, and Svensson C: 'Occupational dermatitis in a Swedish aircraft plant'. *Contact Dermatitis* 1996 **34** 336-340.

13 Jolanki R, Sysilampi M C, Kanerva L and Estlander T: 'Contact allergy to cycloaliphatic epoxy resins'. Current topics in contact dermatitis. Ed Dooms-Goossens A et al. Springer, Berlin Heidelberg New York 1989 360-367.

14 Christopher J and Dannaker D O: 'Allergic sensitisation to a non-bisphenol A epoxy of cycloaliphatic class'. *Journal of Occupational Medicine* August 1988 **30** (8) 641-643.

15 Emmett E A and Kominsky J R: 'Allergic contact dermatitis from ultraviolet cured ink'. *Journal of Occupational Medicine* 1977 **19** 113-115.

16 Kanerva L, Estlander T and Jolanki R: 'Allergic contact dermatitis from dental composite resins due to aromatic epoxy acrylates and aliphatic acrylates'. *Contact Dermatitis* 1989 **20** 201-211.

17 Jolanki R, Kanerva L and Estlander T: 'Occupational allergic contact dermatitis caused by epoxy diacrylate in ultraviolet-light-cured paint, and bisphenol A in dental composite resin'. *Contact Dermatitis* 1995 **33** 94-99.

18 May C A: 'Epoxy Resins, Chemistry and Technology' Second Edition, edited by May, published by Marcel Dekker Inc, New York and Basel, Chapter 4, 1988.

19 Dernehl C U: 'Clinical experiences with exposure to ethylene amines'. *Ind Med* 1951 **20** 541-6.

20 Kanerva L, Estlander T and Jolanki R: 'Occupational allergic contact dermatitis caused by 2,4,6-tris-(dimethylaminomethyl)phenol, and review of sensitising epoxy resin hardeners'. *International Journal of Dermatology* December 1996 **35** (12) 852-856.

21 Kanerva L, Jolanki R and Estlander T: 'Allergic contact dermatitis from epoxy resin hardeners'. *American Journal of Contact Dermatitis* June 1991 **2** (2) 89-97.

22 Brooke R and Beck H M: 'Contact allergy to 2,4,5-tris (dimethylaminoethyl)phenol'. *Contact Dermatitis* 1998 **38** 394-285.

23 Kanerva L, Hyry H, Jolanki R, Hytönen M and Estlander T: 'Delayed and immediate allergy caused by methylhexahydrophthalic anhydride'. *Contact Dermatitis* 1997 **36** 34-38.

24 Foulds I S and Koh D: 'Allergic contact dermatitis from resin hardeners during the manufacture of thermosetting coating paints'. *Contact Dermatitis* 1992 **26** 87-90.

25 Thorgeirsson A: 'Sensitisation capacity of epoxy reactive diluents in the guinea pig'. *Acta Dermatovener (Stockholm)* 1978 **58** 329-331.

26 Tosti A, Guerra L and Bardazzi F: ' Occupational contact dermatitis from exposure to epoxy resins and acrylates'. *Clinical Dermatology* 1992 **10** 133-140.

27 Jolanki R, Estlander T and Kanerva L: 'Contact allergy to an epoxy reactive diluent: 1,4-butanediol diglycidylether'. *Contact Dermatitis* 1987 **16** 1987.

28 Jolanki R, Kanerva L, Estlander T and Tarvainen K: Epoxy Dermatitis, Occupational Medicine, January-March 1994 **9** (1) 97-112.

29 Nishioka K, Ogasawar M, Asagami C: 'Occupational contact allergy to triglycidyl isocyanurate (TGIC Tepic®). *Contact Dermatitis* 1988 **19** 379-380.

30 Munro C S and Lawrence C M: 'Occupational contact dermatitis from triglycidyl isocyanurate in a powder paint factory'. *Contact Dermatitis* 1992 **26** 59.

31 Herbert A and Kaidbey K: 'Persistent photosensitivity following occupational exposure to epoxy resins'. *Arch Dermatology* November 1979 **115** 1307-1311.

32 Wheaf M: 'Epoxide Sensitisation Project', 24 July 2000.

33 Kanerva L, Estlander T and Jolanki R: 'Occupational skin disease in Finland'. *International Articles of Occupational Environmental Health* 1988 **60** 89-94.

34 Jolanki R et al: 'Epoxy compounds as a cause of occupational skin disease'. *Contact Dermatitis* 1990 **23** 243-244.

35 Jolanki R et al: 'Occupational dermatitis from epoxy resin compounds'. *Contact Dermatitis* 1990 **23** 172-183.

36 Nixon R and Frowen K: 'Allergic contact dermatitis caused by epoxy resins'. *Journal of Occupational Health and Safety (NZ)* August 1991 **7** (5) 417-424.

37 McDonald J C: Personal communication.

38 Thorgeirsson A and Fregert S: 'Allergenicity of epoxy resins in the guinea pig'' *Acta Dermatouener, Stockholm* 1997 **57** 253-256.

39 Holness D L and Nethercott R: 'Occupational contact dermatitis due to epoxy resin in a fibreglass binder'. *Journal of Occupational Medicine* February 1989 **31** (2).

40 Van Putten P B, Coenraads P J and Nater J P: 'Hand dermatoses and contact allergic reactions in construction workers exposed to epoxy resins'. *Contact Dermatitis* 1984 **10** 146-150.

41 Goh C L, Gan S L and Ngui S J: 'Occupational dermatitis in a prefabrication construction factory'' *Contact Dermatitis* 1986 **15** 235-240.

42 Irvine C, Pugh C E, Hansen E J and Rycroft R J G: 'Cement dermatitis in underground workers during construction of the channel tunnel'. *Occupational Medicine* 1994 **44** 17-23.

43 Conde-Salazar L, Gonzalez De Domingo M A and Guimaraens D: 'Sensitisation to epoxy resin systems in special flooring workers'. *Contact Dermatitis* 1994 **31** 157-160.

44 Conde-Salazar L, Guimaraens D, Villegas C, Romer A and Gonzalez M A: 'Occupational allergic contact dermatitis in construction workers'. *Contact Dermatitis* 1995 **33** 226-230.

45 Geier J and Schnuch A: 'A comparison of contact allergies among construction and non-construction workers attending contact dermatitis clinics in Germany'. *American Journal of Contact Dermatitis* June 1995 **6** (2) 86-94.

46 Angelini C et al: 'Occupational sensitisation to epoxy resin and reactive diluents in marble workers'. *Contact Dermatitis* 1996 **35** 11-16.

47 Goh C L: 'Common industrial processes and occupational irritants and allergens – an update'. *Annual Acad Med Singapore* 1994 **23** (5) 690-698.

48 John Mowlem Ltd, Visit to Tower Bridge, 25.11.78.

49 Holmes H: 'Allergic contact dermatitis: preventive measures in the building and construction industry'. *Journal of Occupational Health and Safety* (Aust, NZ) 1991 **7** (5) 409-416.

50 Pegum J S: 'Penetration of protective gloves by epoxy resins'. *Contact Dermatitis* 1979 **5** 281-283.

51 APME's Epoxy Resin Committee publication: 'Protective gloves for epoxy resin systems'. Brussels March 1996.

52 Henriksen H R and Petersen S: 'Better gloves against epoxy and other chemicals'. Institute of Chemical Industries, Technical University of Denmark, 1986.

53 Roed-Petersen J: 'A new glove material against epoxy and acrylate monomer'. Current topics in contact dermatitis. Ed Frosch P J, publ Springer, Berlin Heidelburg New York, 1989 603-606.

54 Blanken R, Nater J P and Veenhoff E: 'Protective effect of barrier creams and spray coatings against epoxy resins'. *Contact Dermatitis* 1987 **16** 79-83.

55 McClain D C and Storrs F J: 'Protective effect of both a barrier cream and a polyethylene laminate glove against epoxy resin, glyceryl monothioglycolate, frullania and tansy'. *American Journal of Contact Dermatitis* December 1992 **3** (4) 201-205.

56 The Society of the Plastics Industry Inc: 'Epoxy resin systems safe handling guide'. September 1997.

57 Market and business development. The UK industrial flooring market. July 2000.

58 IAL Consultants, series C. 'The European market for structural adhesives 1999 – introduction, European summary and market by type.' November 1999.

TABLES

Table 1 Forecast European market growth in structural adhesives by type and end-use 1999-2004 (% growth pa) [*57*]

Adhesive Type	Aerospace	Automotive	Domestic Appliances	Electrical & Electronic	General Industry	Marine	Other Land Transport	Sandwich Panels	Total
Anaerobic		1.8	2.1	3.2	2.2		1.3		2.1
Cyanoacrylate		2.1	2.1	3.4	2.6		1.0		2.4
Epoxy film	6.6					2.4			4.9
Epoxy paste	6.0	1.2	3.1	4.8	1.5	1.9	0.6	3.4	1.5
Phenolic	6.1	0.4							1.0
Polyimide	6.1			4.2					5.0
Polyurethane		1.3	3.0		2.7	1.8	0.9	3.2	2.4
Silicone		3.0			3.1				3.0
Toughened Acrylic				3.1	3.9	3.7	1.8		3.1
Other Acrylic					2.0				2.0
UV Curing		2.3		3.5	4.6				3.9
Total	6.4	1.3	2.9	3.8	2.0	2.0	0.9	3.2	2.2

Table 2 Forecast total European consumption of structural adhesives by type and end-use 2004 (tonnes)) [*57*]

Adhesive Type	Aerospace	Automotive	Domestic Appliances	Electrical & Electronic	General Industry	Marine	Other Land Transport	Sandwich Panels	Total
Anaerobic		199.4	69.7	58.5	493.5		34.7		855.8
Cyanoacrylate		259.6	92.2	84.0	204.7		40.6		681.1
Epoxy film	400.0					241.7			641.7
Epoxy paste	168.0	3953.1	220.8	100.9	5124.0	1363.0	687.3	28.3	11645.4
Phenolic	44.3	347.5							391.8
Polyimide	12.1			16.0					28.1
Polyurethane		3884.0	3025.6		3412.0	684.0	4212.0	11271.7	26489.3
Silicone		198.4			111.7				310.1
Toughened Acrylic				34.4	99.2	42.0	72.2		247.7
Other Acrylic					635.0				635.0
UV Curing		9.2		36.7	51.4				97.3
Total	624.4	8851.2	3408.4	330.5	10131.5	2330.6	5046.8	11300.0	42023.4

Table 3 Forecast European market growth in epoxy paste structural adhesive by country and end-use 1999-2004 (% growth pa)) [*57*]

Country	Aerospace	Automotive	Domestic Appliances	Electrical & Electronic	General Industry	Marine	Other Land Transport	Sandwich Panels	Total
Austria & Switzerland		0.2			0.5		0.8		0.5
Benelux	7.0	1.3		5.4	2.3	1.9	-0.7		1.6
France	6.1	1.6	1.9	5.4	1.0	2.2	0.4		1.5
Germany	6.0	1.5	2.3	4.4	1.7	1.4	0.5	3.6	1.6
Italy	5.6	-0.6	3.5	5.4	1.9	2.1	0.7	3.7	1.4
Nordic	6.2	1.2	1.2	7.0	2.3	2.0	0.5		1.7
Spain & Portugal	5.9	1.1	3.7	7.7	2.6	1.9	1.2		1.9
UK & Ireland	5.9	1.2	2.3	3.1	1.7	1.9	1.0	2.3	1.7
Total	6.0	1.2	3.1	4.8	1.5	1.9	0.6	3.4	1.5

Table 4 Forecast segmentation of the UK market for industrial flooring, by type, 2000-2004) [*57*]

Description	2000	2001	2002	2003	2004
Epoxy Resin	16.3	16.2	20.4	21.5	22.3
Polyurethane	10.9	10.6	13.3	14.5	15.1
Cementitious Polymer	5.9	5.9	7.3	8.1	8.4
Methacrylate	1.4	1.3	1.5	2.1	2.3
Screeds	0.6	0.6	0.5	0.6	0.6
Total Seamless	35.1	34.6	43.1	46.8	48.7
Dust Pressed Tiles	4.0	4.0	4.6	5.0	5.1
Mastic Asphalt	0.3	0.3	0.3	0.3	0.3
Chemical Resistant Bricks	0.3	0.3	0.3	0.3	0.3
Total Other Industrial Flooring	0.6	0.6	0.6	0.6	0.6
Total	39.7	39.2	48.3	52.4	54.4

Table 5 Forecast UK market for industrial flooring, 2000-2004) [*58*]

Year	Value	% Change
2000	39.7	-24
2001	39.2	-1
2002	48.3	+23
2003	52.4	+9
2004	54.4	+4

Table 6 Composition of the tested formulations [*48*]

1	**Hardeners**
1.1	Isophorone-diamine + benzyl alcohol (60g + 40g)
1.2	Diethylene-triamine/bisphenol A – Mannichbase, free amine content ca. 40% free bisphenol A ca. 20%
1.3	Polypropyleneoxide-diamine (molecular weight ca. 230) + nonyl-phenol (80g +20g)
1.4	Polyamine adduct in water solution, solid content ca. 80%, free amine content ca. 7% isophorone-diamine ca. 10% polypropyleneoxide-polyamine (molecular weight ca. 400)
1.5	Polyamino-amide based on dimerised fatty acid and triethylene-tetramine, free amine content <1%
1.6	Polyamino-amide based on dimerised fatty acid and triethylene-tetramine, free amine content <1%, 50% in xylene/n-butanol 1/1
2	**Epoxy Resins**
2.1	Bisphenol A+F/epichlorohydrin epoxy resin, ratio 70/30, epoxy value ca. 0.53; diluted in 20% cresyl-glycidyl-ether
2.2	Bisphenol A+F/epichlorohydrin epoxy resin, ratio 70/30, epoxy value ca. 0.53; diluted in 20% ethyl-hexyl-glycidyl-ether
2.3	Bisphenol A/epichlorohydrin epoxy resin, ratio 70/30, epoxy value ca. 0.53; diluted in 20% hexanediol/diglycidyl-ether
2.4	Bisphenol A/epichlorohydrin solid epoxy resin, epoxy value ca. 0.21; in xylene solution, solid content 75%

Table 7 Mechanical performance of various glove materials and estimation of glove price [*48*]

Properties	NR	CR	NBR	Butyl	FR	PVC
Tensile strength (MPa)	25	20	≥40	10-12	8-12	15
Elongation at break (%)	1000	800	500	700	400	300
Tear resistance[1] (N/mm)	≥50	25	20	20-25	15-20	25
Resistance to perforation[2] (N)	15	20	≥50	15	15	30
Glove thickness (mm)	0.5	0.5	0.35	0.5	0.4	0.6
Flexibility at RT	Very good	Good	Average	Good	Average	Poor
Flexibility at low temperature	Very good	Good	Average	Good	Poor	Poor
Comparative price	1	4	3	25	100	3

[1] According to Norm DIN 53515
[2] According to Norm DIN 4841

Table 8 Swelling (S) after 8 hours and break-through time (BT) [48]

Formulation	NR (0.5mm)		CR (0.5mm)		NBR (0.35mm)		BR (0.7mm)		BBR (0.5mm)		FR (0.4mm)		PVC (0.5mm)	
	S (%)	BT (mins)	S (%)	BT (mins)	S (%)	BT (mins)	S (%)	BT (mins)	S (%)	BT (mins)	S (%)	BT (mins)	S (%)	BT (mins)
Hardener 1.1	8.5	47	23	565	19	>480	2	>480	-	>480	2	>480	15	470
Hardener 1.2	3.5	70	2	>480	2	>480	2	>480	-	>480	2	>480	3.5	>480
Hardener 1.3	12	125	23	-	5	>480	2	>480	-	>2480	8.5	>480	5*	>480
Hardener 1.4	3.5	36	3.5	510	2	>480	2	>480	-	>480	2	>480	2	570
Hardener 1.5	2	>480	2	>480	2	>480	<2	>480	-	280	2	>480	2	>480
Hardener 1.6	23	-	23	-	23	360	8.5	350	-	280	2	>480	2*	-
Epoxy resin 2.1	5	53	7	>480	2	>480	2	>480	-	>480	2	>480	3.5	>480
Epoxy resin 2.2	14	48	21	-	7	>480	2	>480	-	>480	2	>480	8.5	>480
Epoxy resin 2.3	3.5	42	5	>480	3.5	>480	2	>480	-	>480	2	>480	3.5	>480
Epoxy resin 2.4	15	14	15	175	15	540	10	625	-	455	2	>480	28	-

* Extraction of plasticiser

Table 9 Typical exposure effects associated with epoxy resin systems [53]

Epoxy resin systems components	Examples/type	Dermal exposure	Inhalation exposure	Ingestion exposure
Liquid epoxy resins	Based on the reaction product of epichlorohydrin and bisphenol A or bisphenol F	Mild to moderate irritants Mild to moderate sensitisers	Low volatility, exposure unlikely unless heated, sprayed or spread over large unventilated surfaces	Low toxicity
Solid epoxy resins	Based on the reaction product of epichlorohydrin and bisphenol A or bisphenol F	Mild to moderate irritants and mild sensitisers Not readily absorbed through skin	Low volatility, exposure unlikely unless crushed or ground	Low toxicity
Modified liquid epoxy resins	Liquid epoxy resins with added reactive diluents or solvents	Mild to moderate irritants Moderate to strong sensitisers	Low volatility, exposure unlikely unless heated, sprayed, or spread over large unventilated surfaces	Low toxicity
Aliphatic and cycloaliphatic amine curing agents		Irritants, sensitisers, corrosive, absorbed through skin	Respiratory irritants	High toxicity
Aromatic amine curing agents		Sensitisers, long term health effects, absorbed through skin	Respiratory irritants	Moderate to high toxicity
Anhydride curing agents		Corrosive, severe sensitisers	Dusts may be sensitisers	High toxicity
Reactive diluents	Glycidyl ethers	Moderate to strong sensitisers	Moderate volatility, exposure possible	Low toxicity
Solvents	Acetone, methyl ethyl ketone (MEK), toluene, xylene, glycol ethers, alcohols	De-fats and dries skin Some may be absorbed May carry other components through skin	High volatility, exposure possible Irritation Central nervous system depression (e.g. dizziness, loss of co-ordination)	Low to high toxicity Long term effects
Fillers	Fibreglass, silicas, calcium carbonate, powdered metal pigments	Some may be absorbed	Dust inhalation	Low toxicity

Table 10 Exposure potential of production processes and tasks [53]

Processes	Exposure Potential*		Comments
	Inhalation	Ingestion	
Filament winding/pultrusion	Medium	Low	
Resin transfer moulding	Medium	Low	
Prepreg and laminate production	High	Low	
Flooring, grouting and hand applications	High	Low	Large surface areas and high temperatures may increase possibility for inhalation exposure
Coating	High	Low	Spraying the coatings causes generation of aerosols which increase the potential for inhalation exposure
Tasks			
Unloading/mixing/pouring • hose connect/disconnect • drum pump cleaning/handling • dumping/pouring	Medium	Low	
Cutting/machining/finishing	High	Low	These tasks generate dust which increase the potential for inhalation exposure
Clean up	High	Low	Potential for hazardous effects increases due to solvent use
Maintenance	Medium	Low	
Spraying	High	Low	Spraying the coatings causes generation of aerosols which increase the potential for inhalation exposure
Brushing	Medium	Low	
Hand layup	Medium	Low	

* Dermal exposure potential for all processes was high.

Table 11 Gloves – chemical resistance generalisations [53]

Epoxy resin systems/ components Generic glove material	Epoxy resins, liquid or solid	Modified epoxy resins	Hardeners/ curing agents	Solvents
Ethyl vinyl alcohol (EVAL) laminate	Excellent	Excellent	Excellent	Excellent
Butyl rubber	Excellent	Excellent	Excellent	Good
Nitrile (NBR)	Excellent	Good	Fair	Fair
Neoprene	Excellent	Good	Fair	Fair
Vinyl (PVC)	Excellent	Poor	Poor	Poor

Notes:
Excellent - breakthrough time >480 minutes
Fair - breakthrough time <20 minutes
Good - breakthrough time >20 minutes
Poor - glove material degradation occurred during testing

Printed and published by the Health and Safety Executive
C1.25 02/03

HSE BOOKS

MAIL ORDER
HSE priced and free
publications are
available from:
HSE Books
PO Box 1999
Sudbury
Suffolk CO10 2WA
Tel: 01787 881165
Fax: 01787 313995
Website: www.hsebooks.co.uk

RETAIL
HSE priced publications
are available from booksellers

HEALTH AND SAFETY INFORMATION
HSE InfoLine
Tel: 08701 545500
Fax: 02920 859260
e-mail: hseinformationservices@natbrit.com
or write to:
HSE Information Services
Caerphilly Business Park
Caerphilly CF83 3GG

HSE website: www.hse.gov.uk

RR 079

£10.00

ISBN 0-7176-2675-X

9 780717 626755