Epoxide Tannage : a way forward

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Abstract

An understanding of both the reactive functions of epoxide resins and collagen, suggests that some epoxides could be effectively used in organic tannage systems. As such epoxides may be regarded as alternatives to aldehydic tanning systems, having lower toxicity combined with specific polymerization ability. The commercial and technical potential of epoxides as tanning agents are assessed in this review paper. To this end, an introduction to epoxide chemistry is provided based on the tanning chemist's viewpoint. The literature survey describes epoxide-protein/collagen addition reaction mechanisms and their kinetics, which in turn are discussed with respect to the potential for future work, where these resins will be utilised in novel tanning technology. The potential risks associated with epoxides and modifications to conventional techniques of tanning, are also discussed.

Keyword : Epoxide, Epoxy, Organic tannage, Aldehyde alternatives, Epoxide-protein reaction, Crosslinking

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Background

Market demand has always been a main impetus for technological development and innovation, and now legislation demands careful environmental considerations as well. For the leather industry at this time, there is more pressure than before to pursue chromium-free, environmental friendly processes and products. Most of the driving force for this comes from the automotive industry. Taking Audi as an example, around 50% of vehicles produced have leather internal furnishing, all which are chrome-free[1]. The same trend is also beginning to appear in other leather sectors. It is not difficult to predict that in the near future, mineral-free tannages will ultimately replace conventional chromium methods, which have prevailed for more than three centuries[2].

Along with the traditional vegetable tannins[3], some organic tanning agents and tannages have developed more recently, e.g. (modified) glutaraldehyde[4], oxazolidine[5], phosphonium (THPS)[6], melamine resins[7]. For the most of the leather produced, two key criterions are difficult to achieve simultaneously:

- high hydrothermal stability,
- negative formaldehyde testing.

Meantime, due to the variations in tannage chemistry, organic tanned leathers usually need more retannage and fatiliquor materials (*cf.* chrome tannages); these are both associated with higher levels of discharge effluent. Therefore a novel organic tannage technology is still eagerly awaited, which will provide a cleaner processing route and better product properties.

Epoxide (epoxy) tannage is not a new idea. The first attempt to use multifunctional epoxide compounds was carried out by Sykes[8], Bitcover[9] and other leather chemists in the 1950s. The leather produced was reported to have a shrinkage temperature of 85°C, with a similar mechanical properties to chrome and vegetable tanned leathers[10]. However, from that original investigation few developments have followed. One exception was work done by Masuoka[11], studying epoxide tannage catalysts in 1987. The lack of development might be explained by the lack of commercial and legislative pressures for a cleaner organic leather technology at that time, as opposed to the alternative, aldehydic tannages being any the more superior with respect to resultant leather properties. It may be suggested that a lack understanding of epoxide chemistry

relevant to a leather chemist's needs, also hindered development. In particular, studies of epoxide polymerization and cross-linking reactions in aqueous environments, would be unusual compared with the typical research involving either organic solvent or solvent-free conditions (e.g. for coatings and reinforced composites, respectively).

Crosslinking and related modification of protein-based materials by epoxides for specific industrial applications, has attracted interest from other researchers. For instance, the protein fibres such as silk (fibroins) [12] and wool (keratin) [13], have been modified with epoxides to improve the crease-resistance and storage performance in textile finishing. To increase mechanical strength, durability and biocompatibility, collagenous bioprostheses[14] have been subjected to fixation using epoxides in tissue engineering; while the epoxide compound is effective for protein immobilization on the insoluble carriers,(e.g. of enzymes, antibodies) [15]; etc. As such, the range of epoxide materials represent relatively minor uses, while over the last 50 years the development and use of commercial epoxide resin has grown rapidly[16], especially in the composites, adhesives and coatings fields. As reactive prepolymers, many epoxides have some distinct advantages over other reactants, including:

- reactive to a wide range of functional groups under suitable conditions
- variety of molecular structures, which may be tailored for specific application methods and/or end uses;
- polymerisation, addition or crosslinking by forming covalent bonds;
- relatively low toxicity;
- fairly freely available in relatively large qualities commercially.

The variety of properties found in epoxides makes them one of the most obvious groups of candidate reactants, to be used as substitutes for the aldehydic tanning agents.

More importantly, according to the "cooperating unit" tanning theory proposed by Covington [17], high hydrothermal stability maybe expected for multifunctional epoxide-based tannage. Using a combination of crosslinkers as tanning agents, such as diamine or polyphenol with an epoxide, might bring about additional polymerisation within a collagen matrix. Leading to a complex three-dimensional network, which is analogous to that produced by vegetable tannin-oxazolidine[18] or melamine-formaldehyde systems.

The main objective of this review is to continue the evaluation of epoxide tannages, that may bring about some innovations to the leather industry. General epoxide chemistry and epoxide-protein reactions are summarized below, along with technical problems associated with epoxide tannage system observed so far. From this, ideas for future practical work will be developed and put into practice.

Epoxide chemistry

The reactivity of the epoxide group

An epoxide (or epoxy) is a heterocyclic compound which is typically characterised by the reactivity of its oxirane ring. The most common type of epoxides are based on the asymmetrically substituted terminal α-epoxy (1,2-oxirane) glycidyl ether [19,20]. Their high reactivity is due to ring-strain, inherent in the three-membered oxirane ring:

The wide range of reactions is summarised in Figure 1. In most commercial applications an epoxide is converted to three-dimensional network structure (i.e. formation of a thermoset), by the reaction with a suitable polyfunctional cross-linking agent (also known as *curing agents* or *hardeners*). Not surprisingly, the reaction rate of any system varies according to the type of crosslinking agent employed, while the properties of the cured polymerisation product are dependent on both of the epoxide and the crosslinking agent used[21]. Normally the term 'epoxide resin' refers to the low molar mass, reactive prepolymer resin, which is either liquid at ambient or a low melting point solid. The solid, full, (usually thermoset), epoxide polymer resins are formed by covalent addition reaction processes, with a variety of suitable cross-linking agent.

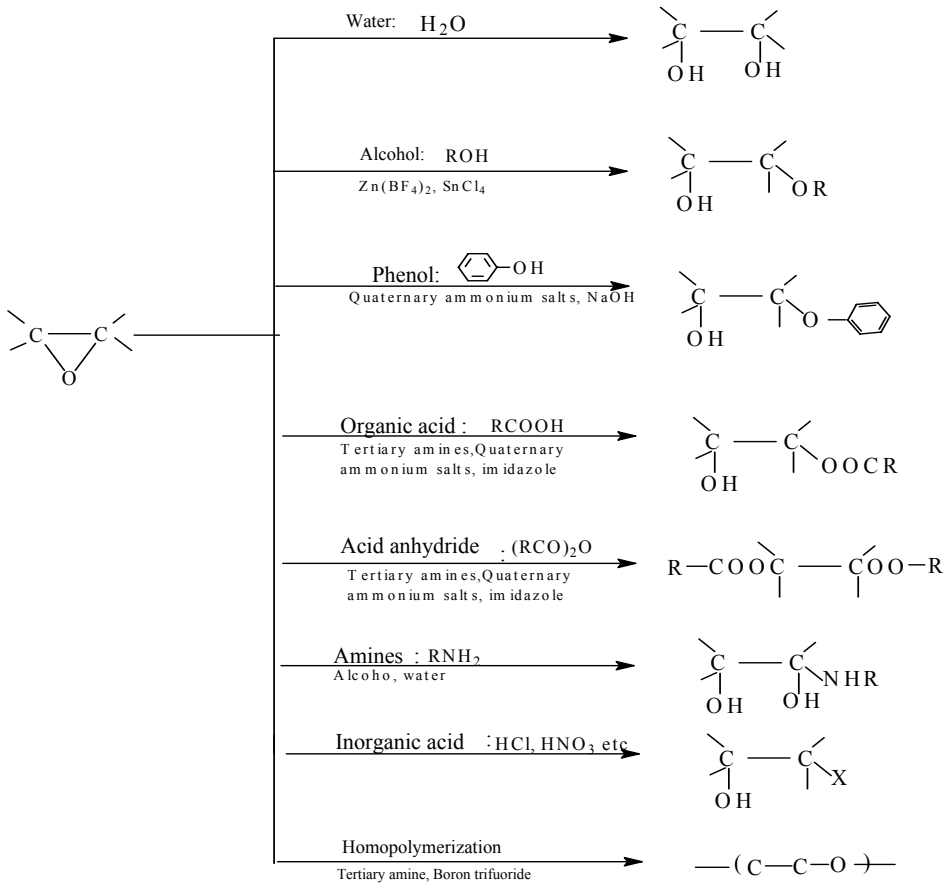
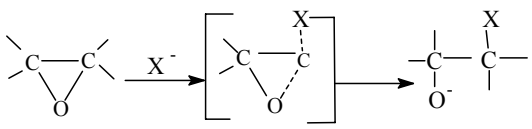


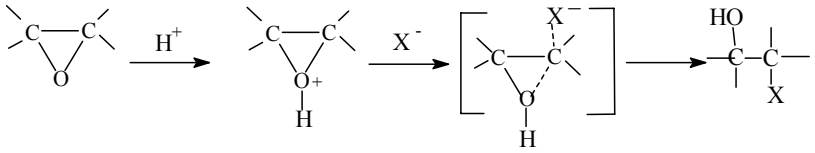
Figure 1 The main reaction classes of the epoxide group

The opening of the oxirane ring involves either electrophilic attack on the oxygen atom or nucleophilic attack on one of the ring carbon atoms[22]. There can be various types of substitution depending on the type of the reagent used. It has been agreed by most researchers[23], that all the oxirane ring opening mechanisms are ionic (i.e. both anionic or cationic), normally in the presence of water, so that the highly polar carbon-oxygen bond can be broken. Both base and acid environments promote the ring open by addition, but by different mechanisms :

a) Under basic or neutral conditions, all ring opening reactions are similar and involve an attack by a nucleophile on one of the carbon atoms of the oxirane group, the procedure is regarded as S_N2:



b) Under acid conditions, the reactions of most types of nucleophile can be accelerated by acid, through the formation of a reactive conjugated acid from the epoxide species, which involves proton attack of the ring's oxygen atom.



As shown in Figure1, an epoxide is reactive to various proton-supplying groups (HR) for the addition reaction. As far as the specific application of an epoxide in tanning is concerned, there are four reactions of most interest: with amine, organic acid, the homopolymerization and the hydrolysis of the oxirane ring. It must be noted that while there have been many kinetic studies and reviews carried out on epoxide curing reactions [24,25], most of this work was carried out using organic solvent medium or do in the bulk (solvent free) states. Epoxide reactions in atypical environments, such as leather tannage conditions, (e.g. typically aqueous phase, narrow pH range from 3 to 9, low reaction temperature<50°C), are far less well understood.

The amine addition is readily carried out. The activation energy of an amine reaction is reported to be 8 to 14 kcal/mole, depending upon the nature of the amine and the method of measurement[19]. Aliphatic amines in particular, require no or little catalyst. The active hydrogen groups of the amine groups accelerate the reaction rate in these systems, as do various hydroxyl-containing compounds to differing degrees, e.g. in the presence of water, isopropanol. The addition of a mole of phenol to the same reactants has been reported to accelerate of the reaction[26]; even when started at room temperature the reaction is likely to rapidly run out of control. Using a model compound, 1,4-butanediol diglycidyl ether (BDDGE) and 4,9-dioxane-1,12-dodecanediamine, the reaction order with respect to the amine groups was found to be 1.20, compared to 0.45 for a non-catalyzed and hydroxyl group catalysed reactions. Further it was observed that especially at lower temperatures, the reaction of a primary amine with an epoxide group is considerably faster than the reaction with a secondary amine group. Aromatic amines are normally found to be slower reactants than the aliphatic types[19]; because the phenyl group has a poorer electron-donating ability, while the higher electron density of the amine group will also increase its reactivity to an epoxide.

The acid-epoxide reaction resulting in esterification, but this normally needs to be activated having the reaction temperature to >100°C, while water, the condensation by-product should be removed because of the reversibility of the reaction - the ester formed tending to hydrolyse[27]. However, the most effective method for promoting reaction is by the use of reaction-specific catalysts, which include alkaline salts, organo-metallic salts, tertiary amines, etc., (see Figure2).

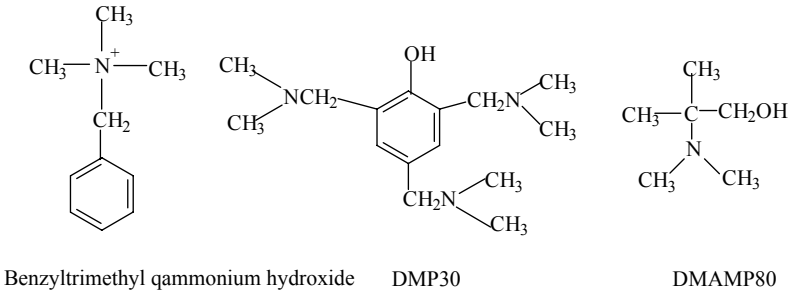


Figure 2 Acid-epoxide esterification catalysts

With catalysts such as tertiary amines (and other Lewis bases or acids), an epoxide also can undergo catalytic curing and crosslink by homopolymerization. A catalyst acts by attacking a carbon atom on the oxirane ring, forming of an alkoxide ion, (see Figure3); an alcohol will function as accelerator in this reaction. Epoxide molecules react directly with each other and the resulting polymer has ether repeat units in its main chains. The amount of catalyst used with an epoxide resin is usually determined empirically, depending on the optimum balance of polymer properties produced under specific processing conditions. DMP30 has been used at concentrations of 4 to 10% with a liquid diglycidyl ether, producing fairly rapid cure rates "over night" at 25ºC, with the resulting thermoset polyethers having a Tg range of 63 to 80ºC [19].

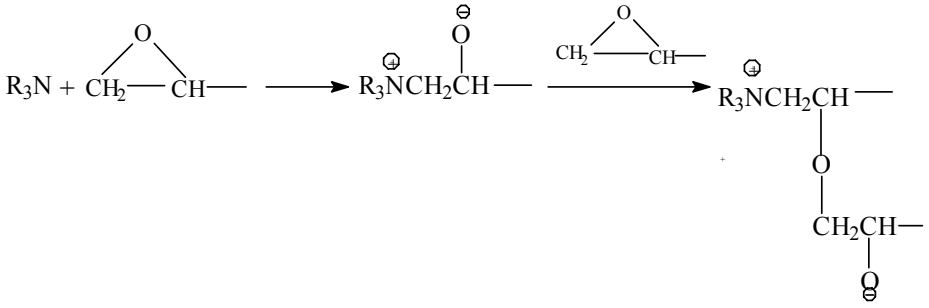


Figure 3 Catalytic homopolymerization procedure

Oxirane rings will gradually hydrolyse for form diols in water; an epoxide resin is particular unstable in acid pH conditions[28]. Epoxides are relatively stable over the range pH6 to 9, while the degree of hydrolyzation is promoted by increasing reaction temperature at low epoxide concentration, (see Table 1).

Table I.

Epoxide stability in aqueous solutions[29]

Temperature	Degree of Hydrolyzation/ %					
	25ºC			40ºC		
Epoxide concentration	***5%***	***10%***	***20%***	***5%***	***10%***	***20%***
24hour	4.0	3.7	3.5	10.5	10	9.5
48hour	8.0	7.0	6.0	21	20	19
144hour	22	20	18	62	59	53

The phenol-epoxide addition also is worthy to note, it is the fundamental of aromatic type epoxide resin preparation and advancement. The addition of phenolic hydroxyl and oxirane is selectively catalysed by basic compounds and *N,N*-dialkylacid amide such as dimethylformamide. Furthermore, there is a strong evidence[30] that plant polyphenol (condensed tannin)-epoxide resin systems behave similarly to tannin paraformaldehyde system, especially at basic pH values.

Commercial liquid epoxide resins

Commercial epoxide resins can be categorized into four classes; (typical molecular structures are shown in Figure 3):

- The most important for industry are the diglydyl ethers or dihydoxyl compounds; about 95% of them are made by the condensation of epichlorohydrin ECH with bispenol A, e.g. DGEBA, (i.e. with a degree of polymerisation of 0); see Figure 3 (I).
- Glycidyl ethers of aliphatic polyols (II) have some water solubility and between 2 to 8 times more active than DGEBA [19]; see Figure 3 (II).

- Because of their high aromatic to aliphatic ratios, epoxidized novolac resins will give thermoset polymers with rigid in main chain structure, further affected by high epoxide group functionality; see Figure 3 (III).
- The cycloaliphatic epoxides usually have low viscosity and prefer to react with carboxyl rather than amine group[31]; see Figure 3 (IV).

With the exception of the aliphatic epoxide resins, the other three types of epoxide resins are commonly employed to produce high thermally stable, polymerisation products.

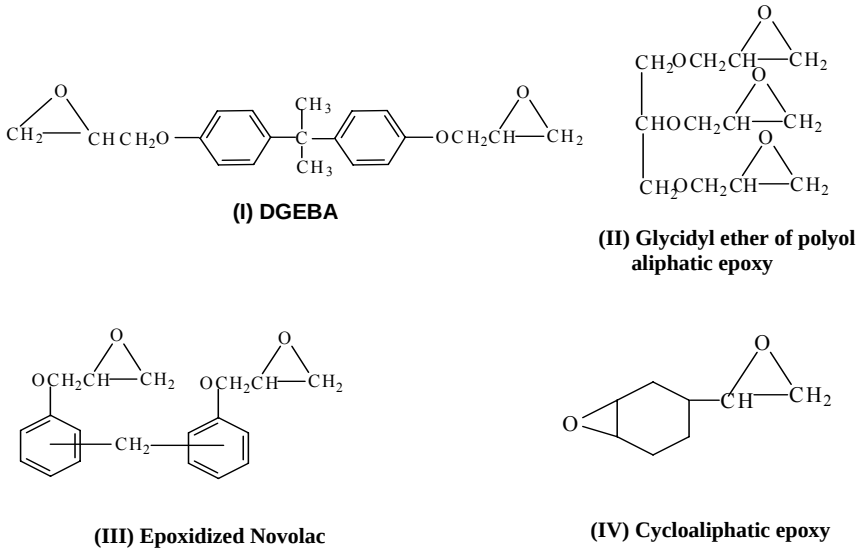


Figure 3 Typical structures of different types of epoxide resins

It should be noted that both ambient temperature curing and waterborne epoxide systems are currently important development areas for the commercial resins industry. The ambient temperature curing types are converted to polymers using high reactivity crosslinking agents such as polyamines and polyamides[23] and with the use of selective catalysts. The waterborne epoxide systems are formulated either to be self-emulsifying or made by phase-inversion emulsification techniques [32,33]; epoxide resins *per se* are not water soluble. Most syntheses techniques are proprietary although many products are commercially available. It is thought many epoxides have the potential to be effective tanning agents, which are either available commercially, or could be specifically synthesized in a laboratory.

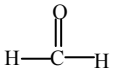
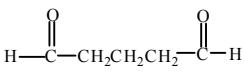
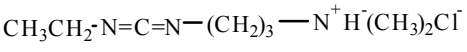
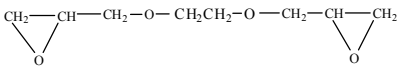
The safety issues related to the use of epoxide resins

With the ability of epoxides to react with protein-based materials outlined above, *it is not surprising that they* can show certain physiological toxicity. In particular, the oxirane group can react with biomacromolecules, such as protein and polysaccharides, causing irreversible chemical modification e.g. through the covalent crosslinking of cells and tissues. However, through the vitro-evaluation cytotoxicity of diepoxy compounds (which are used for biomaterial modification), it has been demonstrated that epoxides are more *biosafe* in the role as crosslinkers, in comparison to formaldehyde, glutaradehyde or carbodiimides[34]; data are shown in Table 2. The maximum non-cytotoxic concentration of a epoxide solution by a medium eluate method is reported to be 55 to 60 ppm, and 150 to 200 ppm by the agar overlay procedure. In comparison, glutaraldehyde is cytotoxic at concentrations as low as 10 to 25 ppm as a solution and as low as 3 ppm in tissue culture[35].

The low molecular weight epoxides may be associated with high vapour pressures at ambient. Therefore epoxide vapours can be absorbed through the skin leading to damage, or by inhalation leading to certain toxic effects. The LD_{50} for butadiene dioxide is 0.078 g/kg, while for DGEBA it is 11.4 g/kg, (i.e. grams per kilogram of body weight) .It should be noted that the epoxide monomer, epichlorhydrin is a highly volatile and toxic[24].

Table II.

Comparison of cytotoxicity of different crosslinkers to L929 Cells

Crosslinkers	NR_{50} *(μg/ml)
Formaldehyde 	1.7 ± 0.2
Glutaraldehyde 	3.9 ± 0.7
EDC 	5.6 ± 0.9
Glycol diglycidyl ether 	19.5 ± 5.7

* NR_{50} is defined as the test specimen concentration at which the cell activity is reduced to 50% of the control.

The addition reaction of epoxy to collagen / protein materials

Reaction mechanisms

As stated, multiple numbers of reaction sites exist as side groups on protein polypeptides, e.g. as amine ($–NH_2$). carboxyl acid (–COOH) and thiol groups (–SH). Therefore there is strong possibility of condensation reactions taking place between protein and an epoxide. With the probability of these reactions taking place in aqueous solution, they may be seen as extensions to the normal crosslinking reactions of epoxides. Difunctional or higher functionality epoxide would be expected to introduce a stabilization effect to collagen, by producing crosslinkings in the protein molecule, similar to aldehydic compounds. In comparison, mono-functional epoxides would be expected to have a mainly masking effect, via mono-point combinations[36], giving limited side branch growth, restricting the mobility of the protein molecules. However, to produce particular chemical change and molecular development in protein, quite stringent conditions need to be observed in processing: this is not a simple matter of the specific distribution and availability of functional groups in the treated protein, determining the specific reactions of epoxide with protein. The range of reactions possible is further complicated, for instance because of the possibility of side reactions, such as epoxide homopolymerization or hydrolysis, (as shown in Figure 4). Therefore for certain protein materials, optimizing reaction conditions have to be established to ensure effective change in those polypeptide materials, e.g. in the case of leather tannage, how specific types of inter-chain crosslinking can be generated, to increase the collagen's hydrothermal stability.

Most researchers accept that addition reactions mainly occur at the basic groups of protein[36,37], such as the ε-NH_2 of (hydro)lysine residue, a strong nucleophile present as a relatively abundant reactive side group. The reaction is favourable in high pH conditions (i.e. pH9 to 10). Amino acid analysis of collagen samples before and after epoxide treatment, shows that the conversion of (hydro)lysine can be between 90 to 95%. Moreover, the increase of shrinkage temperature (Ts) resulting from the epoxide crosslinking, shows the same tendency for amine group to dissociate at basic pH. There is also evidence of methionine[38] and tyrosine participate in crosslinking reaction under ordinary conditions, although neither of them are the main components of collagen.

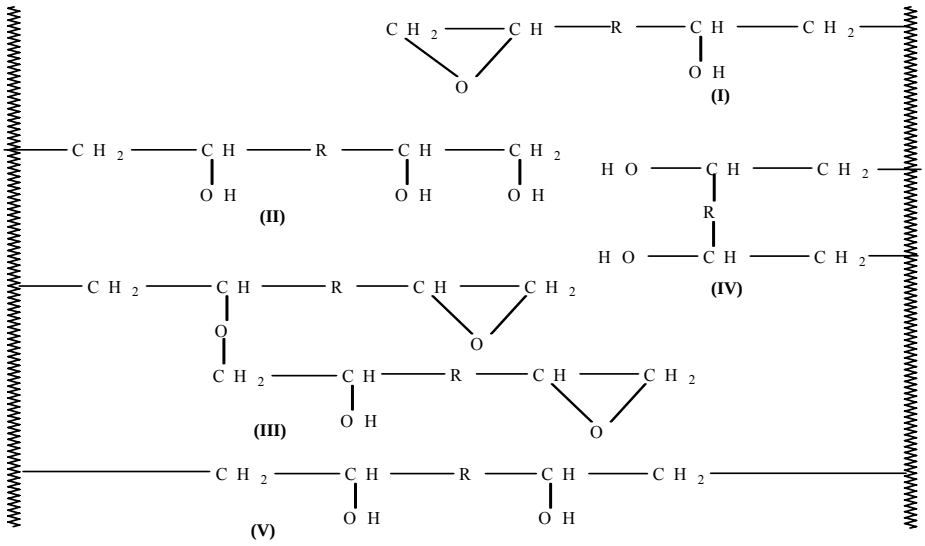


Figure 4 The competitive reactions between difunctional epoxide and polypeptide chain

(I) pendant mono-fixation; (II) hydrolysed mono-fixation; (III) homopolymerization of epoxide; (IV) intra-chain crosslinking; (V) inter-chain crosslinking.

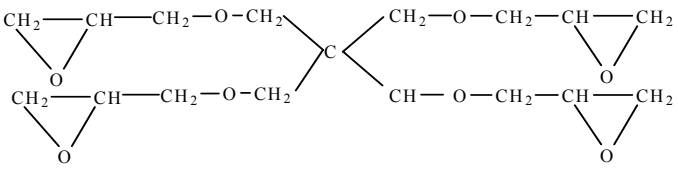
In comparison, the roles of the carboxyl groups of the glutamic acid and aspartic acid components are debatable. A polymer model study has shown that enzyme binding via a –COOH/epoxide reaction is relatively difficult; in comparison, amine groups react easily with the reaction taking place over a range of pH values[39]. Fraenkel-Contrat[40] reported that it was relatively easy to form a ester bond between epoxide and carboxylic acid in the aqueous phase and at low temperatures, the author further suggested epoxides act as effective esterification agents for dissociated carboxyl groups. The reaction of protein with epoxide has been observed to be accompanied with the reaction mixture undergoing a shift in pH towards the alkaline, thought to be a direct consequence of the esterfication of the –COOH. With an epoxide treatment wool shows similar or better dying ability by the acidic dye[41]. An epoxide-crosslinked collagen treated at pH 5, has a reasonable increase of Ts, but reveals very little loss of amine groups with such treatment. An epoxide-treated collagen, subjected to reaction conditions at pH 5 or pH 10, will have different mechanical properties, the former is more flexible and enzyme-degradable, while the latter has properties similar to glutaraldehyde crosslinked collagen[42]. As an epoxide will react readily in both acidic and basic aqueous conditions, the selective reactivity of side chain carboxyl groups needs to be investigated under both situations.

The reaction influence factors

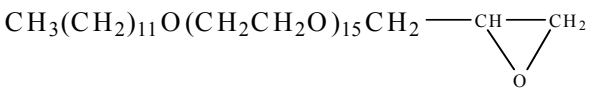
Epoxide's structure

In most studies and applications of the epoxide treatment of protein, the epoxides used have typically belong to the aliphatic class, for instance the condensation products of polyols and ECH, having variable functionality and main chain length. The relationship between epoxide structure and its reactivity to collagen has been discussed by some researchers[43].

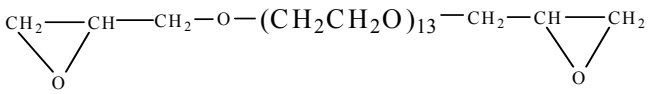
Pentaerythritol Polyglycidyl Ether (EX-411)



Lauryl Alcohol(EO)15Glycidyl Ether (EX-171)



Polyethylene Glycol Diglycidyl Ether (EX-841 n=13)



It has been found that all these type of epoxides have similar fixation rates, as high as 93% (even when an epoxide is used at the same weight of the collagen, with a 4% aqueous solution concentration), which is slightly higher than found with glutaraldehyde (at 0.625% concentration) [36]. On the other hand, these epoxides produce less increase of Ts compared to glutaraldehyde. The degree of crosslinking is in accordance to the epoxide's functionality, with the tetra-functional epoxide, EX-411 showing the highest Ts. However; the degree of crosslinking decreases approximately linearly with the increase of the epoxide's molecular weight (on a logarithmic scale), but in comparison the reduction in crosslinking is not as marked as that found with higher aldehydic compounds. On the other hand, some benefit is gained using epoxides with main chains of higher molecular weight, since additional stability is imparted to the collagen. For example, the mono-functional epoxide EX171, with 45 carbon atoms in its backbone, will elevate the Ts by 11ºC, and difunctional epoxide EX-841, with 32 carbon atoms in

its main chain gives a ΔTs increased by 13ºC. It is thought that a long chain introduced with the epoxide can hinder the mobility of the collagen polypeptide thus bringing extra stability, even if the reaction is at no more than by mono-point fixation. From a kinetics viewpoint, the low molecular mass epoxides provide certain advantages[11].

It is reasonable to suggest that the particular molecular structure of an epoxide's backbone will further influence, e.g. effecting the change of Ts. However, no information has been found in the literature, which compares the differences that an aromatic backbone and an aliphatic backbone have on treated collagen's hydrothermal stability.

pH, epoxide offer, reaction time, temperature and catalysts

The reaction rate of an epoxide with protein, is not as fast as that of many aldehydic compounds. The fixation rate of glutaraldehyde increases rapidly during the first 5 minutes of reaction, while a much longer time is required for epoxide compounds to produce a similar order of fixation. However, after 3.5hr their fixation rates are comparable[44]. A reaction order of 2.5 was observed for a 1,4-butanediol diglycidyl ether-collagen crosslinking reaction[45].

The reaction will be promoted by either higher pH environment, greater epoxide offer (i.e. concentration) in the reaction mass, and/or higher reaction temperature. It is reported that an epoxide tannage at 5% wt reactant concentration and at room temperature, can take longer than 4 days to reach equilibrium, with the most rapid rate of change occurring in the first 24 hours. The reaction time can be shortened to 2 days either if the reaction is carried out at 35ºC [10]. The relationship between the pH and reaction times *vs* collagen's degree of crosslinking (here based on change of Ts with reaction time), is shown in Figure 5. Fast crosslinking is initiated in pH 9.5 to 10.0, the reaction achieving a maximum in 20 hrs. In lower pH reaction conditions, such as 8.5, a maximum takes 140 hrs.

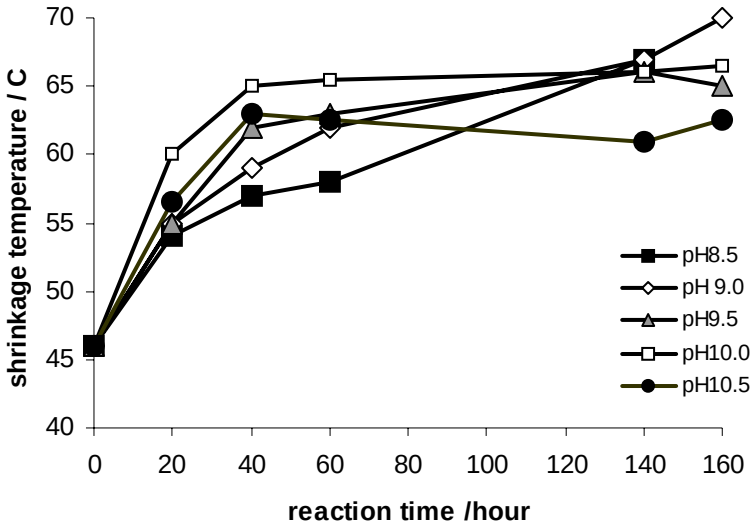


Figure 5 The Ts as function of the pH and reaction time (4% 1,4-butanediol diglydidyl ether , 20°C) [45]

In all probability these reaction conditions would not be accepted for a commercial leather tannage (or by any other industry), when established process conditions (in particular pH, temperature and time), will only tolerate minor variations from the norm, without the collagen starting to degrade or loss of process cost effectiveness. Furthermore, high pH or relatively high tannage temperature will lead to a high degree of masking (i.e. by mono-point fixation), as opposed to crosslinking by an epoxide. For instance, tanning at pH 10.5 and 25ºC will cause 57% epoxide masking in collagen. It has been reported that following a reaction carried out at pH10, the ratio of pendant epoxide groups to crosslinked epoxides was found to be about 1 [46]. In comparison, tanning at pH 8.5 and 25ºC resulted in only 9% of the epoxide being fixed by masking, most of the remaining epoxide groups being involved developing crosslinks[37]. In other words, high pH, high temperature or high epoxide concentration will all contribute to reducing the crosslinking efficiency, but increase mono-point fixation, while accelerating the addition reaction processes. With respect to the reaction environment, pH 9 appears to be the best condition for an epoxide tannage.

Although the best degree of tannage possible with an epoxide, can be achieved by optimization within the acceptable range of reaction conditions, it still falls short of an satisfied degree of crosslinking in a period of the practical leather making process - unless reaction promoting additives are also used. In other words, epoxides alone do not

appear to be as efficient as conventional organic tannages. As such, epoxides can be employed to form intermediate products, but to complete the tanning process and so produce leather with desirable properties, means:

- that other reactive materials (curing agents such as polyamine or polyphenols) have to be used with an epoxide in a tannage formulation or as a combination tannage
- the tannage process may have to be varied to ordinary chrome system, e.g. it can be adapted to high pH tannage system rather than started from pickled pelt.
- Suitable pretannage is preferred to develop a certain initial crosslinks so that stability to collagen, then epoxy tanning can be carried out at either higher temperature or pH than normal process.

One important conclusion stemming from this, is the need to screen a number of types of conventional epoxide catalysts to determine their effectiveness in accelerating fixation and give a high degree of crosslinking. Some work has been done in this area but it appears much more needs to be done to find the most effective catalyst systems.

A few example of catalyst action in epoxide/protein systems have been reported. The use of 2,4,6-trisdimethylaminomethylphenol and salicylic acid, with which the Ts can be raised to over 80ºC, and within the same time scale as currently used commercial chrome tanning procedure[11]. In fact, these catalysts not only promote the addition reaction between epoxide and collagen but initiate the homopolymerization network of epoxide among the collagen matrix. Meanwhile, the catalytic effect of aqueous salt solutions on the epoxide-silk reaction suggests itself as an avenue of investigation. Here in the enzyme immobilization process, high ion strength in reaction solution is used to promote the protein fixation under the conditions of mild pH and at room temperature; conditions selected to avoid deactivation. It has been shown that nucleophilic substitution ability is dependent on the relative catalytic effect of the anion[24]; the order for the salts that used commonly in leather making is:

$$S_2O_3^{2-} > SO_3^{2-} > Cl^- > CO_3^{2} > SO_4^{2-}$$

The properties of epoxide-treated collagen

It has been observed that an epoxide-tanned leather will retain white colouration with ageing. The tanning stability of the resulted leather is retained even after treatment with strong acid or alkali, or organic solvents, such as acetone. This leather also has an unique property of quantitative reversible shrinkage in hot water. It is also reported to have similar properties and thickness as wattle-tanned leather. Tanning with an epoxide resin will result in low stretch and greater stiffness-in-flexure than chrome or vegetable tanned leathers according to the report; it should be noted that the leather sample were tested without any lubrication[8-10].

No published reports have been found that provide comparisons between epoxide-tanned and glutaraldehyde-tanned leathers. Related, relevant information has only been found in biomaterial areas. Di-epoxy-treated and glutaraldehyde-treated collagen have been compared with respect to their mechanical properties, (i.e. tensile strength, elongation at break, and low and high strain modulus), which indicate similarities. The di-epoxy-treated collagen has been reported to more readily retains its moisture content and is more pliable[43]. The reason for these beneficial properties maybe due to the ether bonds (-O-) in-chain, with hydroxyl groups, being incorporated in the collagen matrix with reaction with the epoxide, serving as flexible joints in the crosslinking bridges. In the contrast, glutaraldehyde will only introduce C-C bonds, which are comparatively stiff.

An investigation into post-tannage properties of epoxide-tanned leather, particular dying and fat-liquoring, will be carried out in future work by the authors. These types of material are expected to show better performance than glutaraldehyde types, since reaction mechanisms are varied and result in different IP point of collagen..

Conclusions and future work

Undoubtedly, epoxide resins, or compounds based on them, can provide good alternatives to aldehydic tanning agents. Compared to glutaraldehyde, the epoxides give rise to more complicated reaction mechanisms with collagen, e.g. through crosslinking, mono-point fixation, hydrolyzation and polymerisation. The amine and carboxyl groups of collagen could both participate in addition reactions, although the amine groups are expected to show the greater activity.

An ‘optimum’ epoxide tannage system needs to be establish, based on findings of past research, while exploiting the advantages such resins offer. The wide variety of commercial epoxide resins provides considerable choice of materials for screening studies, where the best types will be identified for collagen crosslinking, and with the intention of selecting new types of commercial organic tanning agents. There is a possibility that epoxides with specific molecular weight, main chain structure and side group functionality will be found ‘off-the-shelf’, meeting criteria proposed in the literature for good tanning agents. However, failing this, new epoxide resins can be synthesized with “tailored” molecular structures. Low temperature curing materials, such as polyamine, should be investigated as ‘co-polymerization agents’, to be used in conjunction with epoxides to maximise process and product properties.

It has been recognised that certain problems have been observed with the use of the few epoxides examined to date:

- Epoxide resins tend to have relatively low reactivity *(cf.* aldehydic tanning agents). It is possible to activate the oxirane ring by use of selective catalysts and reaction conditions, thus promote the tannage finishing in an acceptable time scale.
- The majority of epoxide resins are non-water solubility. It is thought the most recently developed waterborne epoxide systems are likely to provide an answer. It may be suggested that organic solvent based tannages be used, although environment pollution legislation demands a suitable solvent recovery facility be available. It is also thought that attempting to chemically modifying cheap, commercial epoxide resins, such as DGEBA, to meet current tannage requirements, would rather be difficult. The introduction of hydrophilic groups to the molecule usually means loss of an epoxide group and functionality.

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