



The Optimization of Epoxide-based Tannage Systems: An Initial Study

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Abstract

Liquid epoxide resins have an obvious potential as collagen crosslinkers, in particular as alternatives to the aldehydic-types used. In the work reported here, some conditions for the effective use of epoxides in tanning systems have been studied and identified based on hide powder trials.

Few commercial aromatic epoxides are found to be water-soluble, and also have relatively low reaction rates, proving another disadvantage. In a series of screening tests, it has been found that an epoxide with aromatic groups in its backbone, used to treat collagen, produces higher hydrothermal stability than that treated with aliphatic epoxide. However, of the commercial aliphatic epoxide resins examined in this research, the water-soluble, tetra-functional pentaerythritol polyglycidyl ether, (e.g. *Denacol EX 411*), has been shown to be suitable for the leather tannage applications.

Different types of waterborne epoxide resins, including emulsion and emulsifiable resins based on BDEGA (bisphenol A diglycidyl ether), have been examined but gave disappointing results. It is thought that difficulties here lie in trying to achieve good penetration into the collagen's fibrous structure, of the particles that make up such emulsions.

Late stage tannage, giving a leather product with high shrinkage temperature ($T_s = 85^\circ\text{C}$) has been achieved; here the system required catalyst to produce acceptable conversion within 3 hr at 50°C . The important factors influencing the effectiveness of a particular tannage, are discussed.

1. Introduction

Until now the use of commercial epoxide resins or compounds in leather tannage, has not been comprehensively studied. Little work in this area has been reported in the literature since the 50's. Sykes^[1] and Clarke^[2] used di- and tri- functional aliphatic epoxide resins and found the most obvious drawbacks were:

- long reaction time, as long as 5 days;
- relatively low shrinkage temperature, T_s (i.e. below 85°C) of the resulting tanned leather.

A paper by Masuoka in 1993, cast some light on this approach to tanning, utilizing 2,4,6-tris(dimethylaminomethyl) phenol (TDAMP) and salicylic acid as catalysts, while also studying the effects of some other additives, e.g. methanol and ammonia, in the reaction system. A tannage processed this way can increase T_s to over 80°C, within 10 hr. Although the authors suggested in this paper they were to continue this work, nothing further has been found in the literature. In addition, little appears to have been done in adapting their findings from the laboratory scale experiments into practical tanning applications.

On the basis of a thorough literature survey, followed by model compounds studies, the prime objective was to gain a more complete understanding of the mechanisms of epoxide-collagen reactions. Questions have arisen with respect to establishing maximum tanning effectiveness using epoxides, i.e.:

- (1) what are the relative tanning abilities of various types of commercially available epoxide resins? Will an aromatic structure in an epoxide, result in higher T_s values in the leather, compared to aliphatic epoxides?
- (2) what alternative catalysts are there to TDAMP; are these more efficient?
- (3) what is the most economic process to provide an effective and efficient tannage?

One aim of the study reported below was to optimize a tannage process based on currently available commercial epoxides, while identifying their limitations. The work has focused on screening of commercial epoxide resins, catalysts and tannage conditions. Therefore one aim was to identify specific functional groups and molecular structure of an 'ideal' epoxide resin from these findings, so that an epoxide compound(s) could be 'molecularly tailored' by synthesis of suitable precursor materials, as part of a subsequent research programme.

2. Experimental

2.1 Hide powder preparation

White hide powder (pH4), was supplied by *BLC Leather Technology Centre*. It is made from calf skin using BLC's standard method. Briefly, calf skin was pretreated in a series of processes, which included: soaking; unhairing; liming; deliming; bating and pickling; dehydrated with dried acetone; dried under vacuum at room temperature; grinding to a powder. After these steps most of the non-collagenous components had been removed, leaving relatively "pure" collagen.

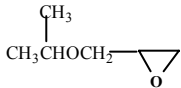
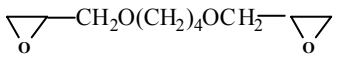
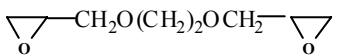
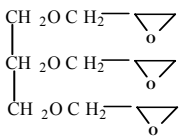
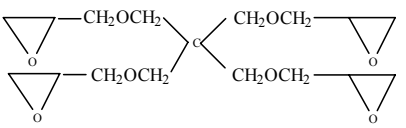
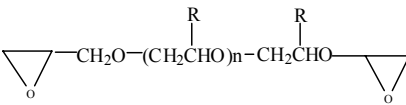
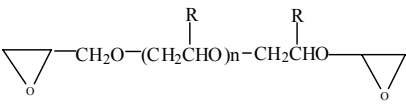
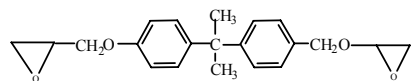
Before the tannage, hide powder (100mg) was soaked in a NaCl (or other sodium salts) solution (3ml, 10% w/v), standing overnight at room temperature, to rehydrated.

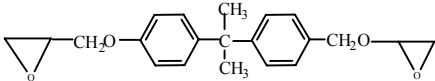
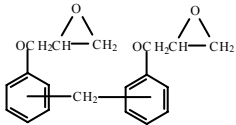
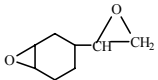
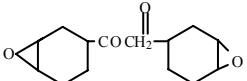
2.2. Epoxide resins

The epoxide resins used in this study were supplied by *Dow*, *Nagase Chemical Ltd* and *Crestchem*, or bought from *Sigma Chemicals*. Their chemical structures and properties are shown in Table 1.

All the epoxides were prepared in acetone to reduce the resins' viscosities, at a concentration of 1g epoxide/1ml.

Table 1 Epoxide compounds used in the study

Epoxide	Structure	f*	Mw	WPE	Viscosity (mPa.s)	Water soluble
(I) Aliphatic Glycidylethers						
<i>Glycidyl isopropyl ether (PGE)</i> From <i>Sigma</i>		1	116	116	-	<input type="checkbox"/>
<i>1,4-Butanedioldiglycidylether (BDDGE)</i> From <i>Sigma</i>			262	131	-	<input type="checkbox"/>
Denacol EX-810 , from <i>Nagase</i> <i>Glycol diglycidyl ether</i>		2	174	112	15	<input type="checkbox"/>
Denacol EX-313 , from <i>Nagase</i> <i>Glycerol polyglycidyl ether</i>		2.5	232	141	145	<input type="checkbox"/>
Denacol EX-614B , from <i>Nagase</i> <i>Pentaerythritol Polyglycidyl ether</i>		4	720	180	4000	<input type="checkbox"/>
DER 732 , from <i>Dow</i> <i>Polyglycol diepoxy</i>		2	610 to 660	310 to 330	550 to 750	<input type="checkbox"/>
DER 736P , from <i>Dow</i> <i>Polyglycol diepoxy</i>		2	350 to 410	175 to 205	300 to 600	<input type="checkbox"/>
DER XZ92465 , from <i>Dow</i> <i>Modified aliphatic liquid epoxide</i>	-			550 to 605	21000 to 29000	<input type="checkbox"/>
(II) Aromatic Glycidylether						
DER 331 , from <i>Dow</i>		2	364-384	182 to 192	11000 to 14000	<input type="checkbox"/>

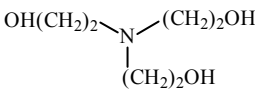
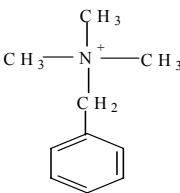
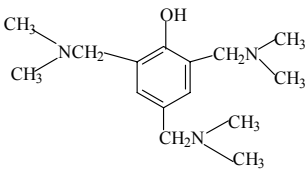
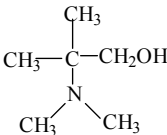
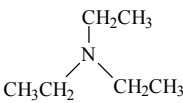
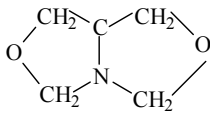
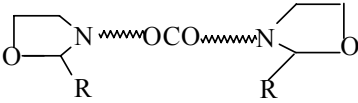
DER331 (Water-based emulsion) , from <i>Dow</i>		2	-	-	-	<input type="checkbox"/>
DER 332 , from <i>Dow</i> <i>Bisphenol A diglycidyl ether (BDDGE)</i>		2	342 to 350	171 to 175	4000 to 6000	<input type="checkbox"/>
DER XZ95381 , from <i>Dow</i> <i>Water dispersible mono-functional aliphatic chain modified bisphenolA/bisphenol F</i>	-	-	-	187 to 193	12000 to 13000	<input type="checkbox"/>
(III) Novolac						
Poly[(o-cresyl glycidyl ether)-co-formaldehyde] , from <i>Sigma</i>		2.7	194	-	10	<input type="checkbox"/>
(IV) Cycloaliphatic						
ERL 4206 , from <i>Sigma</i> <i>Vinylcyclohexene dioxide</i>		2	140	70	-	<input type="checkbox"/>
ERL 4221 , from <i>Sigma</i> <i>3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate</i>		2	252	126	-	<input type="checkbox"/>
(V) Epoxide Blends						
Beckopox EP 147 W , from <i>Crestchem</i> Bisphenol A-ECH (65%) + Novolac 27%		-	-	188 to 200	900 to 1300	<input type="checkbox"/>
Beckopox EP 122 W , from <i>Crestchem</i> BisphenolA-ECH(57%) + Novolac 24% + 2-ethylhexylglycidyl ether			-	190 to 200	70 to 90	<input type="checkbox"/>

The significance of the varying molecular structure of the epoxide resins on conventional polymers, and hence in tanning leather is developed further below in Section 3.2.

2.3 Catalysts and sodium salts

Catalysts and sodium salts were all bought from *Sigma Chemicals*. The structures of catalysts are shown in Table 2. The sodium salts were prepared in aqueous solution.

Table 2 Catalysts used in the study

Catalyst	Structure
Triethanolamine (TEA)	
Benzyltrimethyl quammmonium hydroxide (BTQA)	
Tridimethylaminol phenol (DMP 30)	
2-(N,N-dimethylamino)-2-methyl propanol (DMAMP 80)	
Triethylamine	
1-aza-5-ethyl-1,3-dioxacyclo[3.3.0]-octane (Oxazolidine I)	
Incozol LV (Oxazolidine II)	

2.4 Tannage process

For each reaction study, an excess amount of epoxide resin (100mg) was added to the hydrated hide powder (100mg), with the reaction being carried out using a shaker for 3 days at room temperature, or other times as indicated. The time of 3 days was selected because most reaction systems had reached near-completion after this time, i.e. when the rate of change of T_s , ΔT_s , had slowed significantly. The pH was monitored by a pocket sized pH meter, *checker*® (*Hanna Instruments*), every hour. Where the tannage was carried out in organic solvent phase, water was removed from the hydrated hide powder and replaced by same amount of acetone.

2.5. Determination of degree of tannage

As a means of estimating the degree of tannage, the shrinkage temperature (T_s) of the treated hide powder was determined. Each specimen (~ 10mg) in hydrated form, directly from the reaction medium, was sealed in a standard DSC aluminium pan, and characterised using a differential scanning calorimeter (DSC 2010 *TA instruments*) at the heating rate of 5°C/min, over the range ~ 25 to 100°C; the reference was an empty pan. The endothermic peak temperature observed in the region of the collagen's denaturing temperature, was taken as the T_s of the treated hide powder.

The hide powder tanned in acetone, was washed with clean acetone after the reaction had been stopped, to remove any free, unreacted epoxide, then washed in distilled water and rehydrated in 10% NaCl solution before DSC characterization.

3. Results and Discussion

3.1. Selection of commercial liquid epoxide resins

Chemical versatility is one of the main advantages of epoxide resins. There are many hundreds of them developed by different suppliers and used in a relatively broad range of applications^[4]. Most of these commercial epoxide resins have been either patented or remain as company's priority knowledge.

As indicated in Table 1, commercial epoxide resins basically fall in 4 categories when characterized with respect to chemical structures:

- a) aliphatic glycidyl ethers, which are condensation products of an aliphatic polyol and epichlorohydrin (ECH)
- b) aromatic glycidyl ethers, the condensation products of a polyhydric phenol (such as bisphenol A or F) and ECH;
- c) glycidyl ethers of novolac resin; e.g. poly[(*o*-cresyl glycidyl ether) -co-formaldehyde, which contains aromatic components in its backbone but having been condensed with formaldehyde as opposed to ECH;
- d) cycloaliphatic epoxide with a vinylcyclohexene ring.

It is the second type, the glycidyl ethers based on bisphenol A, that dominate world sales. The thermoset polymers derived from these resins have good mechanical and electrical properties, superior dimensional stability, and good heat and chemical resistance. The mechanical properties stem mainly from the aromatic nature of the bisphenol A segments of the molecule (i.e. acting to stiffen the molecule), and the excellent chemical and thermal stability in part due to the phenolic-ether linkages^[5]. Therefore in this investigation, a standard bisphenol A epoxide resin, *Dow's* DER 331, and a bisphenol A diglycidyl ether (DGEBA, *Dow's* DER 332) have been employed. The main difference between the two resins is that DER 332 has the higher purity, with a maximum epoxide equivalent weight of 176.

The aliphatic glycidyl ethers are sometimes called “flexible epoxides”. They can be used as reactive diluents and flexibilizers, for instance blended into bisphenol A epoxide resins. Research on the collagen-epoxide treatment has been mainly based on these types of epoxides, because they have the properties of water solubility and low viscosity. A series of aliphatic epoxide resins, with several molecular weights and functionalities (*f*) are available from *Nagase Chemicals* under the trade name, *Denacol*. More common resins, such as polyglycol diepoxide, with longer backbone chains are available from *Dow* and other companies, e.g. DER 732 and 736.

The advantage of epoxidized novolac resins is that they can be used to obtain both high cross-link density and thermal stability in thermoset polymers. Such resins can have higher unit epoxide content than DGEBA, (up to 3.6 epoxide groups per molecule) and have an aromatic backbone. However, residual formaldehyde combined with high viscosity, could lead to problems if used in tannage.

Cycloaliphatic epoxides, e.g. ERL 4221 and ERL 4206, because of their high cost are less commonly used, and then for high performance products, providing a combination low viscosity in the reactive form and excellent high temperature resistance in the crosslinked material. An important factor about ERL 4206, is that both amines and anhydrides can be used to cure it. The epoxide on the cyclohexane ring is more reactive under acidic conditions, whereas the epoxide-ethyl group is more responsive to amines^[6]. These properties are attractive in a tannage, because there are both acid and basic side chains on collagen peptides, hence there is seen to be a potential to achieve the maximum degree of crosslinking with an epoxide. However, there are shortcomings associated with this type of epoxide, including comparable higher toxicity and cost.

Currently there are two main trends in the development of epoxide resins:

- waterborne systems,
- low temperature curing systems,

both of which are required in tannage applications. By nature most commercial epoxides are not water soluble. Therefore to achieve water dispersibility the present choice is ^[7]:

- a) use of a handful of (aliphatic) epoxides which are water soluble;
- b) bisphenol A epoxide resins blended with polyamide curing agents have been used as water dispersible systems commercially;
- c) use of ionic or non-ionic modified epoxides to give water-dispersed emulsions.

The water emulsion, *Dow's* DER 331, and two products from *Cretchem*, Beckpox 147 and 122 w, were used in these studies.

3.2 The relationship between epoxide types, structures and their tanning effects

In most respects, leather tannage is regarded as a chemical process in which additional crosslinks are introduced to the collagen molecules. This is clearly an important step to bring chemical and physical stability to the collagen material, irreversibly converting a putrescible hide or skin into a stable leather^[8]. The tanning effect or the degree of crosslinking for a treated collagen can be generally followed by measuring:

- the increase of hydrothermal stability of collagen, expressed as the *elevation of shrinkage temperature* T_s (ΔT_s), or *denaturation temperature* of the protein;
- the increase of biochemical stability of collagen, expressed as *decreased enzyme degradation*.

ΔT_s has been the key parameter used in these studies to screen the epoxide samples and comparing their tanning abilities. It must be remembered that the prime objective of this project has been to obtain a high hydrothermal, organic leather with $T_s > 85^\circ\text{C}$.

Table 3 The T_s of hide powders treated by the epoxides*

<i>Epoxide</i>	<i>Aqueous tannage</i>		<i>Acetone tannage</i>	
	<i>T_s / $^\circ\text{C}$</i>	<i>Tanning effect</i>	<i>T_s / $^\circ\text{C}$</i>	<i>Tanning effect</i>
<i>Control</i>	67		66	
PGE	59	—	59	—
BDDGE	67	—	79	+
Denacol EX-810	80	+	80	+
Denacol EX-313	83	+	82	+
Denacol EX-614B	85	+	84	+
DER 732	72	+	73	+
DER 736p	75	+	75	+
DER XZ92465	64	—	N/A	+
DER 331	65	—	88	+
DER 331 water emulsion	58	—	N/A	+
DER 332	65	—	90	+
DER XZ95381	66	—	85	+
Epoxidized Novolac	64	—	83	+
ERL 4206	64	—	78	+
ERL 4221	64	—	65	—
Beckopox EP147W	55	—	76	+
Beckopox EP 122W	70	—	77	+

*all the tannages were carried out under the same conditions: epoxide offer of 200%wt to the hide powder, at pH 10.0 and room temperature for 3 days.

** — indicates the result was negative or no change compared to control, + indicates a positive result

In comparison, an original, untanned collagen material usually has a T_s in the range 60 to 64°C, while glutaraldehyde-tanned and vegetable tannin-tanned leathers have T_s values < 85°C. The screening results are shown in Table 3.

These results show:

(1) Only in the homogeneous, soluble tanning system does the multifunctional epoxy has the tanning effect

Non-water soluble epoxides, such as DER 331 or 332, have been shown here to react with collagen when dissolved in a suitable organic solvents medium. However, neither the water emulsion of DER 331 nor the water dispersible epoxides showed any ability to produce a reaction. DER 331, one of *Dow's* development products, is a water dispersed emulsion with a fine particle size averaging about 0.3 microns^[9]. In comparison, the typical dimensions of a collagen molecule (i.e. as the triple helix of a peptide chain), is only 1.4nm with the length of 290nm, and microfibril 4.0nm (see Table 4). So since most of the hydrothermal stability is known to be produced by intra-or inter-chain crosslinking of collagen molecules, it may be argued that due to scale differences between particles and collagen molecules, it is difficult to imagine effective crosslinking will occur. Molecular alignment at short distance (i.e. at the molecular scale of 10's of nm) leading to a significant amount of covalent or even hydrogen bonding interactions, is likely to be minimal. Apart from scale differences, questions will arise as to whether any suitable, reactive functional group are available on the particles' surfaces for the emulsion types of tanning agents.

(2) Use of an epoxide with an aromatic backbone, can give slightly higher hydrothermal stability to the crosslinked collagen, *cf.* an aliphatic epoxide.

It has been long accepted in polymer chemistry and physics, that aromatic structure in a polymer's structure provides for greater thermal stability, than comparable aliphatic types^[10]. Then according to Covington's tanning theory^[11], the introduction of steric hindrance into its molecular structure, is one necessary factor to increase the stability of collagen. Thus tanning agents which introduce short, rigid, covalent crosslinks, will give higher T_s values and tanning effects,

compared to epoxide molecules which are based on chains which are long, flexible and have labile bonding. There is strong evidence from the data for DGEBA and aliphatic epoxides, that a Ts of $\sim 89^{\circ}\text{C}$ is possible using the former type and $\sim 84^{\circ}\text{C}$ for the latter. However, it should be noted, their reaction rates are different and an aromatic epoxide will be slower to achieve the degree of conversion and the maximum Ts under the same conditions, (see Figure 1). To this end, it has been found necessary to carry out the collagen-DGEBA reaction at an elevated tannage temperature of 50°C , (see Figure 2).

Table 4 The sizes of different collagen components and leather chemicals^[12]

Collagen-molecule (= triple helix = protofibril)	D = 1.4nm, L = 290nm
Microfibrils (= 5 collagen-molecules = supercoil)	D = 4.0nm
Fibril (≈ 140 microfibrils)	D $\approx 100\text{nm}$
Fibre (= 200 to 300 fibrils)	D $\approx 5000\text{nm} = 5\mu\text{m}$
Fibre bundles (= 30 to 3000 fibrils)	D = 0.02 to 0.2mm
Fat molecule	L = 4 to 5nm
Micro-emulsion	D = 60 to 80nm
Emulsion	D = 100 to 800nm
Vegetable tannin extract	D = 1 to 500nm
Vegetable tannin molecule	D $\approx 4\text{nm}$

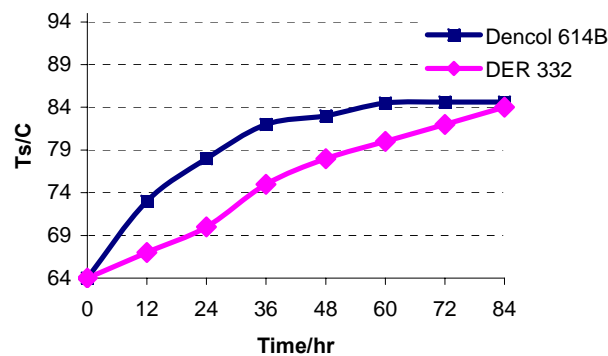


Figure 1 Change in Ts when tanning with epoxides at room temperature

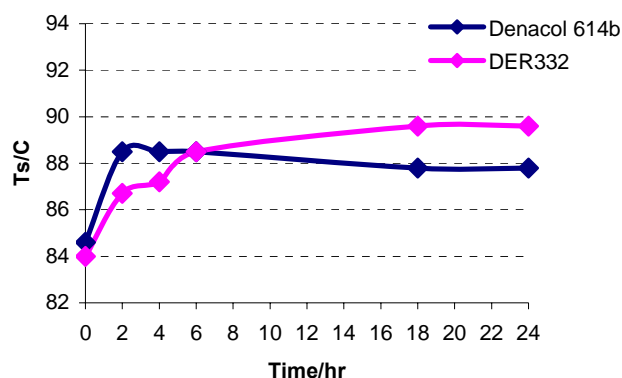


Figure 2: Change in Ts when tanning with epoxides at elevated temperature (50°C)

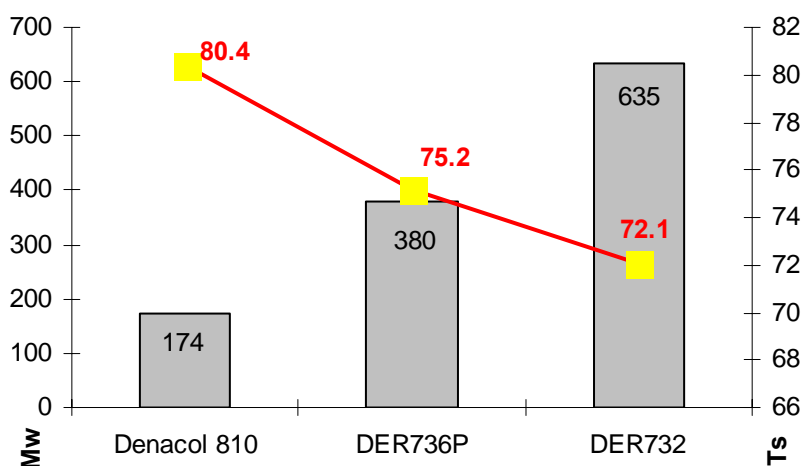


Figure 3: Relationship molar mass of an epoxide and its effect on the resulting leathers

(3) Ts is increased employing epoxides with higher functionality (f) and lower molecular mass.

From the four water soluble aliphatic epoxide resins examined here, the relationship between the Ts obtained has been found to depend on the epoxide's functionality is, i.e. for good hydrothermal stability a multi-functional epoxide should be employed. The tetra-functional Denacol EX 614B gave the highest Ts, while the mono-functional epoxide actual lowered the hide's Ts value, i.e. worsened it. On the other hand, tanning ability is seen to be reduced with increasing epoxide molecular mass, e.g. comparing the polyglycol diglycidyl ethers with different degree of polymerisation, Dencacol EX 810, DER 732, DER 736P, then it is Denacol EX 810 which gave rise to the highest Ts. These findings are accordance to those found in literature^[13,14]. It also has be observed, not

unexpectedly, that the reactivity of an epoxide is reduced with the increasing molecular size, e.g. Denacol EX 614B is kinetically slower than 810, (see Figure 3).

3.3 The Optimum tannage conditions

As stated previously an epoxide tannage has certain advantages over conventional systems, an epoxide may react with more types of functional groups on the protein side-chain, (e.g. $-\text{COOH}$ of glutamic acid and aspartic acid, the phenolic $-\text{OH}$ of tyrosine and even methionine^[15], in addition to the basic groups such as $-\text{NH}_2$). Different reaction mechanisms are possible dependent on the reaction environment selected, (e.g. different pH or temperatures, as well as other reaction condition differences). Considering there are relatively more acidic groups present on the collagen polypeptide, a thorough understanding of epoxide chemistry may be expected to lead to some chromium alternatives.

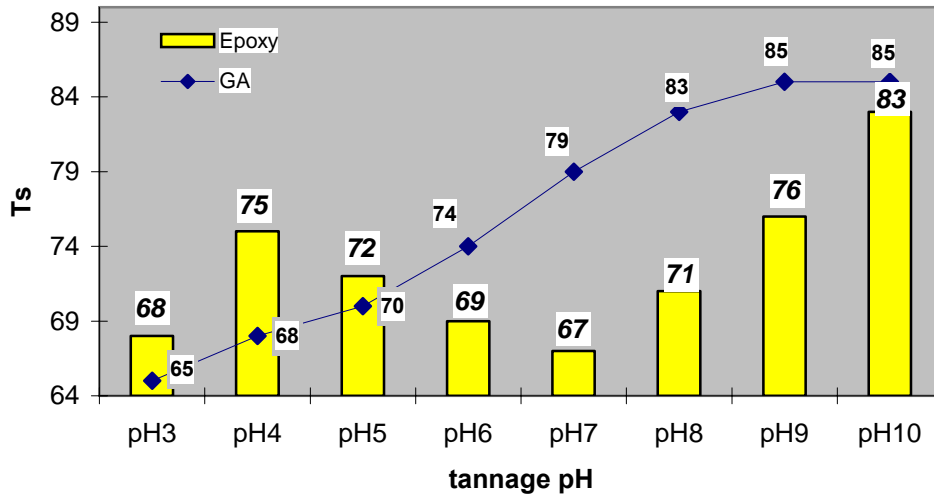
When comparing the Ts results for epoxide-, oxazolidine- and glutaraldehyde-tannages, values are quite close (around 85°C), if the former is allowed to react for long enough. Unfortunately compared to the two aldehydic compounds, the epoxide used showed the lowest reaction rate. This problem stems from the chemical nature of the epoxide group, but the reaction can be accelerated by applying specific catalysts, and under optimised conditions. This part of the investigations was one of our main objectives, investigating the use of the tetra-functional aliphatic epoxide resin, Denacol EX 614B.

3.3.1 Effect of tannage pH

Medium pH of the epoxide tannage system has three influences:

- acidic ($\text{pH} < 6$) or basic ($\text{pH} > 9$) conditions accelerate the hydrolysis of the epoxide group^[16];
- acidic pH or basic pH catalyses the epoxide addition with active hydrogen compounds^[17];
- the availability of $-\text{COOH} / \text{COO}^-$ ($\text{pK}_a = 4$), $\text{NH}_2 / \text{NH}_3^+$ ($\text{pK}_a = 10$) in collagen is decided by medium pH.

From Figure 4, we can see that there are two values of maximum Ts for epoxide treated collagen, i.e. 83°C at pH 10 and 75°C at pH4, while the lowest Ts was found at neutral pH. The results are very interesting in comparison to those for glutaraldehyde, which gave a Ts maximum for pH 9, while losing its reactivity in acidic conditions. This could be explained by the different reaction mechanisms generated by these crosslinkers.



Notes: 1. Tannages were carried out in 1.0N phosphate buffer, RT, for 2 days.

2. GA = glutaraldehyde.

Figure 4: The relationship of tanning pH to resulting degree of crosslinking (related to Ts)

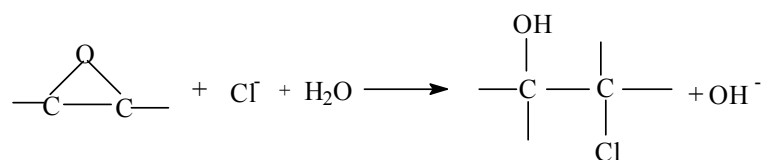
For aldehydic compounds, the main reaction sites are thought^[18] to be at the basic residues, such as lysine, arginine and histidine in their un-protonized states. In the case of epoxide group, acid catalyses the reaction by converting the epoxide into a highly reactive, protonated epoxide, while base catalyse the reaction by converting the lysyl ϵ -NH₂ into stronger nucleophilic reagents. According to our model compounds study^[19]:

- at pH 4, the reaction occurred between –COOH and epoxide;
- at pH 10, the reaction mainly occurred at the –NH₂; –COO[–] also could be involved but the degree of reaction degree is low.

The Ts value resulting reaction conditions at pH 3, is low probably due to the great loss of epoxide groups at this environment.

3.3.2 Effect of salts

Salt treatments are commonly used in the leather industry. For instance sodium chloride (NaCl) and sodium sulphate (Na₂SO₄) are used to cure and store the hide, and inhibit the swelling of a pelt under acidic conditions. Sodium bicarbonate (NaHCO₃), sodium bisulphite (Na₂S₂O₃) are used to increase the pH of tanning system. Pickled hide, the starting process material for most tannages, can have a high content of salt about 10% wt. Generally speaking, salts do not normally have much influence on conventional current tanning processes, however, some these anions have a strong tendency to react with the epoxide group, even at room temperature; a typical example is NaCl. In neutral aqueous solution, Cl⁻ acting as a nucleophilic reagent will attack and broken the epoxide ring releasing -OH⁻, which will increase the pH of the system to 10 in 2 hours.



To summarise, there are three effects caused by NaCl in epoxide tannages:

- break down the epoxide ring and loss of some of the epoxide groups;
- increase of the system's pH, hence promoting the epoxide-collagen reaction;
- stabilization of the collagen structure.

Table 4 Ts of epoxide tanned leather with different amount of sodium chloride

NaCl concentration	Ts of Collagen /°C	Epoxide-treated Collagen		Δ Ts /°C
		Ts/°C	Final pH	
0	56	71	7.5	+15
1.6%	57	71	9.7	+14
3.2%	55	73	9.93	+18
5%	59	79	9.96	+20
6.6%	69	86	10.06	+17
8.2%	70	80	10.08	+10
10%	72	78	10.17	+6

Therefore, although the free Cl^- is usually be seen as a retardant for conventional epoxide curing reactions^[20], it does have the function of catalysing to the tannage reaction under the suitable conditions. The best concentration has been shown to be to 5 to 6% wt, as can be seen in Table 4. However, while high tannage pH is good for achieving maximum crosslinking and Ts, it maybe also lead to damage of the hide structure and hence loss of mechanical properties in the leather obtained.

Table 5 Influence of anions on an epoxide tannage

Sodium salt /1N	En ^{[21]*}	pH of solution	pH with epoxide**	Starting pH of tannage	Ts/°C
<i>NaCl</i>	1.24	7.14	10.46	4.10	86
<i>NaNO₂</i>	1.73	7.30	11.00	4.88	68
<i>NaNO₃</i>	0.29	7.16	7.27	4.10	78
<i>NaHCO₃</i>		7.50	8.70	8.58	73
<i>NaAcetate</i>	0.95	7.71	10.37	6.85	85
<i>NaH₂PO₄</i>		3.93	4.31	3.72	72
<i>Na₂CO₃</i>	1.1	10.42	10.77	10.22	82
<i>Na₂SO₄</i>	0.59	7.25	7.78	4.08	77
<i>Na₂SO₃</i>	2.57	9.50	13.04	8.41	62
<i>Na₂S₂O₃</i>	2.52	8.36	12.94	4.46	66
<i>Na₂HPO₄</i>		9.26	9.24	8.08	85

* Edwards parameter, which indicates nucleophilic substitution reactivity

** Mono-functional epoxide PGE, 0.5N.

As shown in Table 5, the nucleophilic substitution ability of anions can be described by the Edwards parameter, EN. The data here also shows the influence of salts on the tannage reaction. The salts can be divided into three types:

- strongly basic: Cl^- , NO_2^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} ,
- produce no change in pH and hence Ts: SO_4^{2-} , H_2PO_4^- , HPO_4^{2-} , NO_3^- ;
- weak basic salts: acetate, HCO_3^- , CO_3^{2-} .

It has been found that these salts can act in quite differing ways depending on initial reaction conditions. For example, 1.5N Na_2SO_3 destabilizes the collagen, while at

0.5N concentration of Na_2SO_3 , the Ts can be as high as 92°C . $\text{Na}_2\text{S}_2\text{O}_3$ acts powerfully in a negative way, causing reaction system pH to increase to 13 while Ts is reduced by 14°C (cf. Cl^- used as the control). It is thought there is a possibility to select a combination of salts as the pretreatment of the hide, in order to accelerate the subsequent tannage.

3.3.3 Effect of catalysts

The catalysts for epoxide addition reaction are specific according to the reactants. As the addition mechanism is of the ionic type, the catalysts are typically acid or base (or Lewis acid and Lewis base) types by nature:

- for the acid-epoxide reaction, inorganic alkaline salts (e.g. Na_2CO_3), organometallic salts (e.g. lithium stearate) and basic organic compound (e.g. tertiary amines, phosphines and imidazoles) are used;
- for the amine-epoxide reaction, alcohol or water act as catalysts;
- for the alcohol-epoxide reaction, catalysts include $\text{Zn}(\text{BF}_4)_2$ and SnCl_4 ;
- for the phenol, quaternary ammonium salts and NaOH are used;
- acidic catalysts are unsuitable to use, as the epoxide-collagen reaction here will only occur at high temperature, untypical of normal tannage processes, which would result in the degradation of the fibres; (Note: similarly for strong base such as NaOH)^[21].

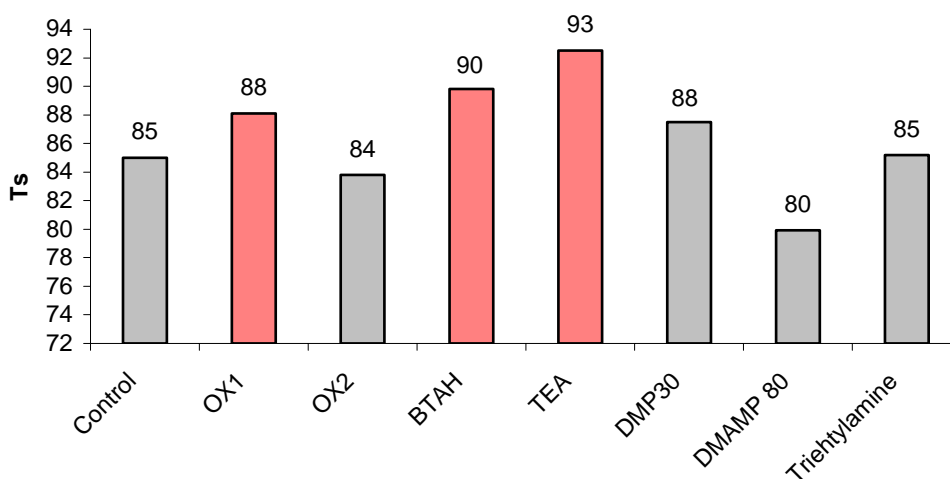
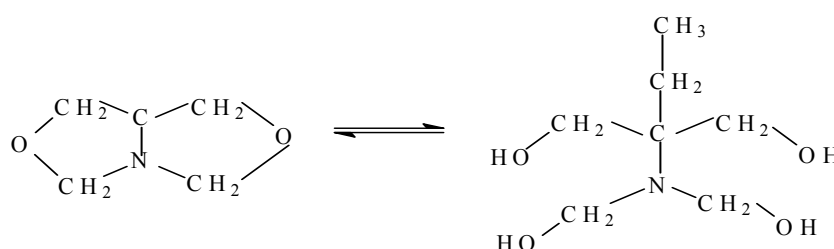


Figure 5: The effect of catalysts on the tannage using epoxide resin

Therefore the search for suitable catalysts has focused on the tertiary amines, based on the requirements of:

- high efficiency,
- weak base,
- water solubility,
- no/low toxic.

The results for this part of the research are shown in Figure 5. The amounts of catalysts used in the tannage system have been generally been low, at 5% wt of the epoxide resin. Benzyltrimethyl ammonium hydroxide (BTAH) and triethanol amine TEA were most effective in increasing T_s , compared to other tertiary amines. In particular, TEA appears to be the most suitable catalyst for this type of application. Oxolidine 1 has also been investigated as a catalyst: although used elsewhere as a commercial tanning agent: on hydrolysis it forms a tertiary amine structure that can be used to promote the collagen-epoxide reaction with active $-\text{CH}_2\text{OH}$ groups^[22].

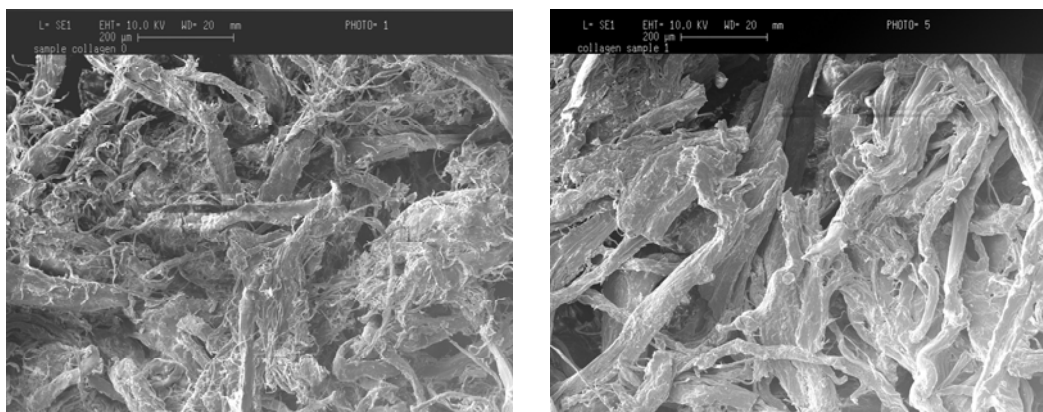


3.3.4 Effects of time, temperature and epoxide concentration

The kinetic factors, time, temperature and reactants' concentration are interrelated. At room temperature, the epoxide reaction is tens-fold slower than glutaraldehyde's to achieve the same degree of crosslinking. The treatment usually takes a few days rather than the several hours for the aldehydic tannage. The $-\text{NH}_2$ -epoxide reaction can take place at room temperature but complete curing only occurs after 7 days, with an uncatalyzed system. The degree of conversion in esterification for a $-\text{COOH}$ -epoxide system has been found to be only about 30% at 50°C for 48hr^[19]. Unquestionably, the an epoxide-based tannage needs catalyst and preferably under elevated temperature and relative high epoxide concentration, for a practical leather process. In reality it is not practical to initiate the tannage process much above 20°C (i.e. used for current

curing processes), because the denature temperature of untreated collagen may as low as 50 to 60°C. However, as the collagen gains increasing thermal stability with tanning, i.e. as soon as the T_s of treated collagen is $\geq 70^\circ\text{C}$, it will be possible to progressively increase the tannage temperature to 50°C over time. Thus the whole tannage could be shortened to an acceptable time, e.g. around 1 days.

When studying the collagen reaction using hide powder, it has been necessary to use considerable greater amounts of reaction medium, (i.e. the aqueous epoxide system), than would be normally employed, therefore the absolute epoxide offer factor could not been determined accurately. In most of these experiments, an excess of the epoxide resin (based on 100% wt. of collagen and 5% of tanning liquid) and a sodium chloride-based medium were used to maximize crosslinking. The results are shown in Figure 2; as can be seen here, the tannage can be conducted successfully at room temperature within 24 hours or better still, operating at 50°C for 3 hours. T_s values have been found to decrease from a maximum, as tannage time at high temperature tannages are prolonged, indicating some deterioration of the collagen's structure.



(a) Untreated collagen

(b) Collagen crosslinked with epoxide

Figure.6 The SEM photomicrographs of collagen before and after epoxide treatment

3.4. The morphology of epoxide-treated collagen

The hide powder's morphology was found to have changed after epoxide treatment, with the tanned product's character and appearance similar to aldehydic-treated samples. The SEM photomicrographs in Figure 6 show a comparison of collagen fibres before and after epoxide-treatment. The fibrous structure of the collagenous

material becomes more compact with the treatment. Further information about mechanical and physical property changes, will only be obtained after small skin trials.

4. Conclusions

By use of hide powder experiments, multi-functional epoxides have been shown to react with and crosslink collagen, thus have certain tanning ability. However, it has been found that a collagen-epoxide reaction needs be carried out in a homogeneous medium and be catalysed, in order to achieve a tanning effect similar to aldehydic tannage.

The screening of a range of commercial, liquid epoxide resins, has shown that an aromatic epoxide will impart higher hydrothermal stability in collagen than an aliphatic epoxide. However, aromatic epoxides have the shortcoming of not being water soluble, while water is the most commonly used solvent in tannage. Different types of waterborne epoxide resins, (emulsions and emulsifiable epoxide resins based on BDEGA) have been examined without finding any benefits. It is thought that it is difficult for emulsion particles to penetrate into the collagen's microfibrillar structure at high enough concentration. Even if this occurs, questions arise as to whether the reactive functional groups of the epoxide are available to react with the collagen's amino-acid functions. Further, the relative slow rates, associated with the kinetics of aromatic epoxide resins, is also another disadvantage.

Allowing for the advantages of aromatic epoxides in enhancing Ts, but combined with their reactivity problems, it has been demonstrated that water soluble, low molar mass epoxides with polyfunctionality are likely to produce the most significant increase in Ts in leather by practical tannage. Therefore, certain commercial, aliphatic epoxide resins, for instance the tetra-functional pentaerythritol polyglycidyl ether (Denacol EX 411), have been shown to be the most suitable for the leather tannage applications. Based on an improving knowledge of epoxide structures to produce more effective tannages, epoxides will be synthesized in the future to test these concepts.

An epoxide tannage has been shown to be accelerated by:

1. careful choice of the initial tannage pH;
2. use of sodium chloride and some salt combinations to pre-treat the collagen;
3. some tertiary amines as catalysts;
4. tannage temperature should be raised to 50°C for 2 or 3 hrs in the later stages of conversion.

An acceptable tannage can be achieved using suitable epoxide resins (i.e. Ts up to 85°C, with tannage finished within 1 days), following these conditions. However, small skin trials are necessary to confirm that these concepts are valid in real tannage processes.

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