Tannins/Melamine–Urea–Formaldehyde (MUF) Resins Substitution of Chrome in Leather and Its Characterization by Thermomechanical Analysis

C. Simon, A. Pizzi

ENSTIB, University of Nancy 1, Epinal, France

ABSTRACT: A new sulfonated melamine–urea–formaldehyde (MUF) resin of relatively low melamine content, prepared according to a sequential formulation, has been shown to be highly effective when coupled with different natural vegetable tannins to produce leather with the same good characteristics of leather prepared with chrome salts. In particular, the antishrinkage effectiveness of the leather prepared according to the new approach is comparable to that obtained with chrome tanned leathers. The comparison of the traditional leather shrinkage temperatures test method with a new thermomechanical analysis (TMA) test method in tension yields thermograms presenting three major modulus of elasticity (MOE) peaks. These are closely connected to molecular level phenomena determining the shrinkage temperature of leather. The three determining parameters appear to be as follows: (1) The average value of the temperatures at which the three MOE peaks occur: the higher the value of this average, the lower is the shrinkage of leather. (2) The average of maximum MOE values of the TMA peaks: the higher this average is, the better is the leather in regard to antishrinkage effectiveness. This means the leather maximum MOE at each peak is a measure of the resistance to the contraction force induced by heat. (3) The relative intensity of the first TMA peak in relation to the second: the higher the value of the MOE for the first TMA peak is in relation to the second peak, the lower the leather shrinkage appears to be. However, it has not been possible to better define or quantify this latter effect. This new TMA test method in tension has also yielded a mathematical relationship correlating the thermogram peak temperatures and MOE averages with the traditional shrinkage temperature to a high degree of confidence. A previous TMA test method, in compression, has proven to yield more problematic and finally not very reliable results when one needs to apply it to a wide variety of different cases. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1889–1903, 2003

Key words: leather; thermomechanical analysis; test methods; chrome substitution; vegetable tannins; melamine resins; shrinkage temperature; tanning agents

INTRODUCTION

The leather tanning industry is one of the most ancient in operation. Although the technology of leather manufacturing has evolved over centuries, and even in recent years, the basic principles for the production of leather have remained the same. Hide proteins, mainly collagen, are rendered insoluble and dimensionally more stable by treatment with chemical products able to fix on them and render them both more resistant to mechanical wear and less susceptible to biological and other types of attack. The main products used today for leather tanning are as follows: (1) acid salts of trivalent chrome, mainly used for the manufacture of soft leathers for shoe uppers and for leather bags; (2) forestry-derived, natural vegetable tannins, such as chestnut and flavonoid extracts, mainly used for the manufacture of heavy, rigid, and hard leathers for shoe soles, saddles, belts, and other implements subject to high wear; (3) aldehydes—in particular, formaldehyde and glutaraldehyde; (4) sulfonated synthetic polymers such as acid phenol–formaldehyde novolak-type resins; and (v) a number of other synthetic resins and compounds (acrylates, oxazolidines, aminoplastic resins, etc.).

Each of the products mentioned above is more apt than the others for the manufacture of certain types of leather. The fact remains, however, that the first two in the list account for more than 90% of all the leather manufactured today, and that the process based on trivalent chrome salts accounts by itself for about 70% of the total. Chrome tanning is particularly suited for soft leather as it does not affect the hide's flexibility and renders the leather very lightfast and very stable both chemically and physically. It produces leather of excellent antishrinkage ability, as indicated by its high shrinkage temperature in testing. The forestry-derived vegetable tannins have instead a strong astringent effect (they fix very effectively on the collagen structure) and give considerable "body," hardness, and toughness to the leather produced with them, but these have the considerable disadvantage to have

marked darkening problems when exposed to light and even worse to shrink at a much lower temperature. It is these two main disadvantages that have somewhat limited their application in relation to the ubiquitousness of chrome salts. Conversely, some synthetic resins such as melamine–urea–formaldehyde (MUF) resins, give light-colored leathers presenting high resistance to degradation induced by light, but none of the other advantages characteristic of chrome or vegetable tanning.

The problem is that chrome salts in general are becoming less acceptable in many types of industry due to potential effluent pollution. Furthermore, well-defined quality standards in regard to leather-product skin-contact allergic reactions have also been introduced for finished products—for instance, in leather clothing and interior car linings. In this respect, two of the requirement limits to comply with are the amount of both leachable trivalent chrome, which generally does not constitute a problem, and of one of its tanning derivatives, namely the more dangerous, highly toxic hexavalent chrome (recent norms[1] limit severely the proportion of hexavalent chrome in leathers to be used in direct contact with human skin, such as watch straps, shoe uppers, etc.). Furthermore, the treatment of tanning wastewaters represents one of the major problems in the leather industry, especially today, as the relevant directives[2] impose ever more stringent effluent limits. The wastewaters are generally treated to abate (never eliminate) chrome salts residues. However, it has proved difficult to find suitable alternatives to chrome-salt leather up to now.

In the case of natural tannins, their capacity of photooxidation limits their use to applications where such a characteristic is of no consequence. It is the phenolic structure itself of the tannin that renders photooxidation possible,[3, 4] but it has also been shown that this effect can be drastically limited if the tannins are condensed with sulfited synthetic aminoplastic resins. Conversely, while the use of synthetic aminoplastic resins is developing in the tanning industry as they give leather a certain degree of softness and flexibility, and they are particularly suitable for coloring, their weak point is the excessive and inevitable presence of free formaldehyde[5] and their poor tanning capability due to their low astringency. Polyphenolic vegetable tannins are well known to act as powerful free formaldehyde scavengers, as they react rapidly and irreversibly with formaldehyde.[4,6] Their combination with aminoplastic MUF resins would markedly reduce the photooxidation of vegetable tannins by synergy with the synthetic resin, would reduce formaldehyde emission to just about zero, would yield a relatively soft but also tough leather, and would eliminate the need for chrome salts. This was indeed achieved for both tanning and retanning, and the relevant results are reported elsewhere.[7] However, the main un-

known with this approach was what type of shrinkage temperature would the new vegetable tans/MUF resin leather present. Failure to at least match the chrome salts performance on this parameter alone would render all the other advantages inconsequential.

Thermomechanical analysis (TMA) has already been used and found to be suitable to characterize collagen biomaterials,[8, 9] although the literature on the subject is indeed very scant[10]; particularly on leather, it is restricted to just one paper.[10]

This article then deals (1) with the development of a new highly effective sulfonated MUF resin for leather tanning of higher performance and lower cost than those commercial today, derived and adapted from resin technology in another field of application[6,11–16]; (2) with the shrinkage temperatures obtained by traditional testing methods on the leather prepared with a variety of different commercial hydrolyzable and flavonoid tannins coupled to this MUF resin; and (3) with a new approach in developing a TMA test capable of yielding good correlations with, and predictions of, the traditional leather shrinkage temperature.

EXPERIMENTAL

The vegetable tannin extracts used for this study were industrially produced, commercially available ones. Two polyflavonoid tannins and a hydrolyzable tannin were used. All three of them are the most used commercial ones for leather manufacture. Of the polyflavonoid tannins, unsulfited mimosa tannin extract, from the bark of the black mimosa tree (*Acacia mearnsii* formerly *mollissima*, de Wildt) ex Tanac (Brazil) and sulfited quebracho tannin extract, from the wood of the quebracho tree (*Schinopsis balansae*) ex Indunor (Indusol Ato type, Argentina), were used. The hydrolyzable tannin extract was chestnut tannin, from the wood of the chestnut tree (*Castanea sativa*) ex Silva (Italy). All the tannins were in the form of spray-dried powders easily dissolvable in water.

Experimental sulfonated MUF resin formulation (example of MUF [M+U]: F 1:1.8 molar weight, M:U 20:80 molar weight)

To 269.6 parts of Formurea (a precondensate containing urea 23%, formaldehyde 54%, water 23%) are added 57.9 parts urea and 71.1 parts of water. The pH is set at 10–10.4 and the temperature brought to 92–93°C under mechanical stirring. The pH is then lowered to 7.8 and the reaction continued at the same temperature, allowing the pH to fall by itself over a period of 1 h and 30 min to a pH of 6.5–7 (the pH must never fall below 5!!!), or otherwise by addition of diluted formic acid. To bring the pH to 9.5 or higher, 22% NaOH solution is added, then 71.1 parts of mel-

amine premixed with 37.2 parts of water. Two parts of dimethylformamide is then added to the reaction mixture, maintaining a temperature of 93°C. The water tolerance is checked every 10 min while the pH is allowed to fall by itself. When the water tolerance reached is 180–200% (the pH reached is around 7.2), 35.5 parts of urea is added and the pH is again brought up to 9.5. The reaction is continued until the water tolerance reached is lower than 150% (the pH has reached 7.7 at this stage).

The pH is then corrected to 9.5 again and 7% of a solution of sodium bisulfite 40% is added on the total weight of resin, and then the resin cooled and stored. These resins, which previously had been used in their unsulfonated form and only for applications other than leather, were characterized by ^{13}C-NMR, and their spectra have already been reported elsewhere.[6, 7, 17]

Commercial old-style sulfonated MUF resin formulation (MUF [M+U] : F 1:2.5, M:U 80:20)[18]

This MUF resin is produced with a molar ratio (M+U):F = 1:2.5. To 126 parts of melamine (1 mole) are added 30 parts urea (0.5 moles), 30 parts of a sodium bisulfite solution (25% in SO_2; 0.25 moles), 240 parts of 30% formaldehyde solution, and 0.2 parts of a 50% sodium hydroxide solution. The initial pH is set to 9 and the temperature increased in 15 min to 80°C under continuous mechanical stirring, and maintained at this temperature for 45 min. The reaction mix becomes clear after 20–25 min of reaction. At the end of this period, 40 parts monoethanolammine (as a stabilizer) are added and the reaction mixture is cooled down to 40°C in approximately 10 min. During this cooling period 25 parts of anhydrous sodium sulfate is added. The resin is then cooled and stored.

Leather tanning procedure

The hides to be tanned were weighed (weight = x), and 1.6 x parts by weight of water on hide weight were added, to which had been predissolved a given quantity y of vegetable tannin extract. The pH was adjusted to 5 and the whole was continuously shaken overnight in a laboratory-sealed revolving tanning drum at ambient temperature. A quantity z of MUF resin was then added to the tanning cylinder, the pH readjusted to 5 with a 8.5% formic acid solution, if required, and the whole shaken continuously for 4 h at 50°C in a laboratory-sealed revolving tanning drum. The total by weight was then x parts of pelt, 2 x parts of tanning solution, and 1.6 x parts of water. The relative proportions y and z used were as shown in Table I.

TMA: Tensile stress measurements

Samples of tanned leather were tested dynamically by thermomechanical analysis. Triplicate leather sam-

TABLE I
Proportions of Materials for Tanning Procedure

Tannin solids/MUF	Tannin (g) y	MUF (g) z
90/10	0.36 x	0.04 x
75/25	0.3 x	0.1 x
50/50	0.2 x	0.2 x

ples, for a total sample dimension of 14.5 × 5.5 mm with a changing thickness between 0.5 and 1.8 mm depending on the leather thickness were stamped with a sample punch and fixed in clamps by two screws with the help of an assembly jig.

These samples were then tested with a Mettler 40 TMA apparatus in tensile stress measurements exercising a force of 0.1 / 0.5 N on the specimens with each force cycle of 12 s (6 s/6 s). The classical mechanics relation between force and dimensional change $Y = (\Delta F\ L_0)/(A\ \Delta L)$, where A is the prompted sample area and L_0 the sample length would allow the calculation of Young 's modulus Y for each of the cases tested.

The experiments with this approach were carried out from 25 to 250°C with at a 10°C/min heating rate, yielding information on the interactions between the tanning solution and the hide, the formation and degradation of the internal network, and the degradation of the hide.

TMA: Measurements by the tension method adapted to the model in ref. 10

Samples of the same dimensions as above were tested according to the compression method model developed in ref. 10. The conditions were the same as the previous tests, but the method, in tension, was based on a curve of percentage shrinkage as a function of temperature where the interval considered is the T_g region comprised between a temperature T_1 and T_2—namely, the extrapolated onset and end temperatures of the T_g region, and the third parameter is the temperature T_r defining the temperature of maximum rate of relaxation, corresponding to the peak of the first derivative of the curve in Fig. 10.

Classical method for shrinkage temperature determination

Samples of tanned leather were tested in the wet state, just after tanning. Triplicate leather samples, for a total sample dimension of 50 × 3 mm for a thickness less than 3 mm were hung on hooks in tension, linked to a weight of 120 g by a metallic wire. The moving of the weight as a consequence of leather shrinkage is evaluated by the rotation of a needle. Thus, when the leather sample is placed in water over a hot plate/magnetic stirrer, the shrinkage of the sample, reached

at a certain temperature, is directly linked to the rotation of the needle, while a thermometer allows us to note the temperature of shrinkage of the leather sample. The system used is codified in the International Norm[20] for Leather I.U.P./6.

Correlation of the relevant TMA temperature and modulus of elasticity (MOE) peaks with the shrinkage temperature of all the leathers prepared was carried out by multivariate linear and nonlinear modeling, and by an iterative Levenby–Marquardt polynomial approximation method.[19]

RESULTS AND DISCUSSION

The two MUF resin formulations show considerable differences. The old style, commercial resin has a very high melamine content (almost 80% by weight on total resin solids) and it is prepared with a nonsequential procedure—hence leaving premixed urea and melamine to freely compete for the available formaldehyde. If it is considered that under any conditions melamine is approximately ten times more reactive with formaldehyde than urea, this means that melamine, in this resin even in molar excess, will be the one mainly reacting with formaldehyde and that most of the urea will not, or will react very little. Such a resin is then almost a pure melamine–formaldehyde (MF) resin in which a considerable amount of unreacted, or very little reacted urea is present. Nonsequential MUF resins formulations have already been proven in other fields to be much less effective resins for a variety of applications,[6,11–15] and to waste usage of the very expensive melamine. The commercial MUF resin formulation is then quite clearly an obsolete one, which is most widely used possibly only as a consequence of the somewhat conservative attitude of a traditional industry such as leather tanning. Usage of this formulation coupled with vegetable tannins did give some improvement as well, but by far not good enough to satisfy either lightfastness or especially the required antishrinkage leather characteristics wanted (results not reported here).[21]

The new MUF resin instead is based on a sequential formulation of proven high effectiveness in several fields[6,17]—hence a formulation where both melamine and urea are added sequentially to ensure their coreaction: they are really both coreacted in the resin and both participate in its formation. It contains a much lower content of the expensive melamine (less than 45% by weight on total resin solids, almost half than the older formulation). It is the development of this resin that has allowed the following results.

Classical determination of leather shrinkage temperature

The results obtained from the classical test method to determine leather shrinkage temperature are shown in

TABLE II
Shrinkage Temperatures Obtained by the Classical Test Method of Experimental Leathers Prepared by Vegetable Tannins/MUF Experimental Resin Mix Containing Different Percentages of Experimental MUF Resin
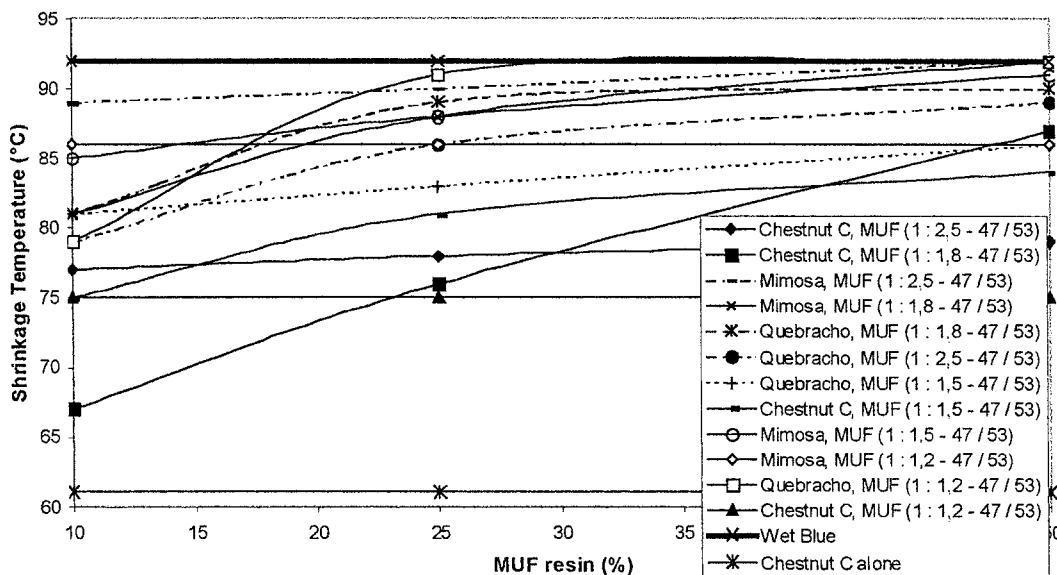
% MUF	Shrinkage temperature (°C)		
	10	25	50
Chestnut C, MUF (1:2.5 47/53)	77	78	79
Chestnut C, MUF (1:1.8 47/53)	67	76	87
Mimosa, MUF (1:2.5 47/53)	89	90	92
Mimosa, MUF (1:1.8 47/53)	81	88	92
Quebracho, MUF (1:1.8 47/53)	81	89	90
Quebracho, MUF (1:2.5 47/53)	79	86	89
Chestnut C, MUF (1:1.8 30/70)	72	73	75
Mimosa, MUF (1:1.8 30/70)	77	84	87
Quebracho, MUF (1:1.8 30/70)	80	83	86
Mimosa, MUF (1:2.5 20/80)	76	91	92
Chestnut C, MUF (1:2.5 20/80)	69	71	75
Quebracho, MUF (1:1.5 47/53)	81	83	86
Chestnut C, MUF (1:1.5 47/53)	75	81	84
Mimosa, MUF (1:1.5 47/53)	85	88	91
Quebracho, MUF (1:2.5 20/80)	81	82	83
Quebracho, MUF (1:2.5 30/70)	83	83.5	84
Mimosa, MUF (1:2.5 30/70)	83	87	89
Chestnut C, MUF (1:2.5 30/70)	71	73	78
Quebracho, MUF (1:1.8 20/80)	81	85	87
Chestnut C, MUF (1:1.8 20/80)	70	75	76
Mimosa, MUF (1:1.8 20/80)	80	88	90
Mimosa, MUF (1:1.2 47/53)	86	86	86
Quebracho, MUF (1:1.2 47/53)	79	91	92
Chestnut C, MUF (1:1.2 47/53)	75	75	75
Wet blue	92	92	92

The MUF and tannin proportions reported are MUF resin solids:tannin extract solids. Chestnut alone: shrinkage temperature = 61°C. Mimosa and quebracho alone: shrinkage temperature = 65°C. Chrome treated wet blue (4.8% chrome): shrinkage temperature = 92°C.

Table II. The first result immediately evident is that at the 50:50 VegTan:MUF solids content ratio there are several formulations that have the same shrinkage temperature as the heavily chrome tanned wet-blue hide (4.8% chrome)—namely, 90–92°C. This is a very positive result. Furthermore, there are several formulations that have a shrinkage temperature very close to that of the chrome-treated control, but at a 75:25 Veg-Tan:MUF solids content ratio, and there is even one formulation at 89°C shrinkage temperature at a 90:10 VegTan:MUF solids content ratio. There is then a variety of formulations to chose from that are capable of overcoming the major drawback of vegetable tanning in relation to chrome tanning.

The general trends in Table IX follow.

1. The polyflavonoid tannins perform here better than the hydrolyzable chestnut tannin, with mimosa presenting in general a slightly higher shrinkage temperature than quebracho. This difference in performance in this parameter be-
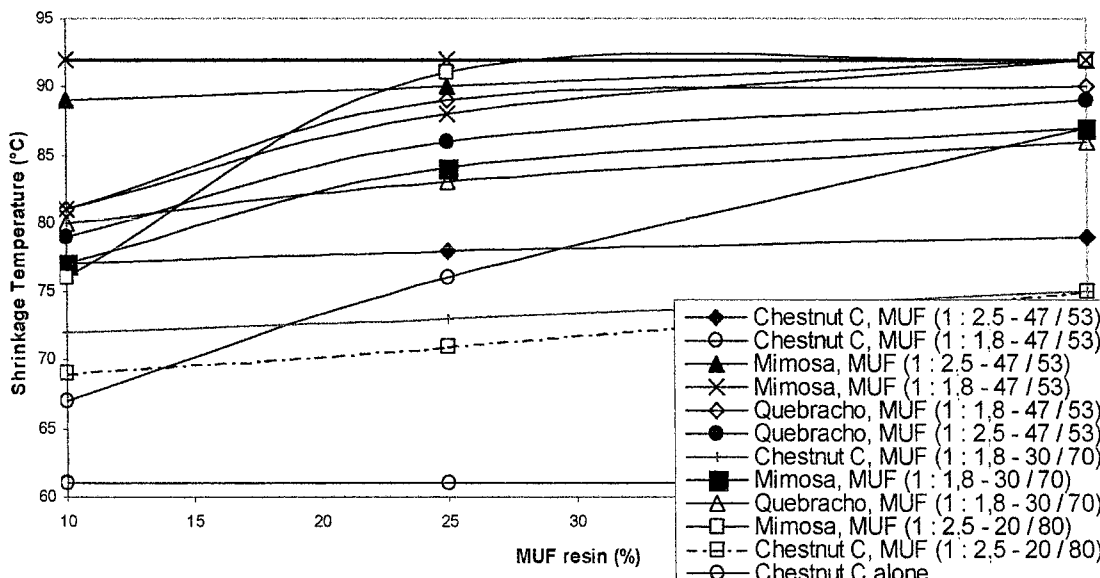
Figure 1 Example of leather shrinkage temperatures as a function of the percentage MUF resin solids on total solids formulation in the tannin/MUF tanning formulation for different tannins and different (M+U):F molar ratios. MUF resin has M:U = 47:53.

tween flavonoid and hydrolyzable tannins is logical if one considers the following: (a) Tannin and MUF can coreact together by interaction of the MUF methylol groups with the reactive phenolic nuclei of the tannins, and (b) flavonoid tannins are far more reactive than chestnut tannins toward any methylol group.[4] There is greater interaction between the flavonoid VegTan and the MUF during and after tanning of the hide than in the case of chestnut tannin. Thus, there is a higher proportion of copolymerization networking between tannins and MUF when using fla-

vonoid tannins than in the case of the slower reacting chestnut tannin. The extent of formation of interpenetrating networks during curing is then likely to be lower in flavonoid tannins. It must be pointed out that one of the 50:50 chestnut:MUF treated leathers still presents the excellent shrinkage temperature of 87°C, thus not far at all from chrome tanned leather.

2. In general, but not always, at the highest MUF content (the 50:50 cases), the higher the MUF molar ratio (with again very little or no difference between 1.8 and 2.5) and the higher the propor-

Figure 2 Leather shrinkage temperatures as a function of the percentage MUF resin solids on total solids formulation in the tannin/MUF tanning formulation. MUF resins have M:U of 47:53, 30:70, and 20:80.
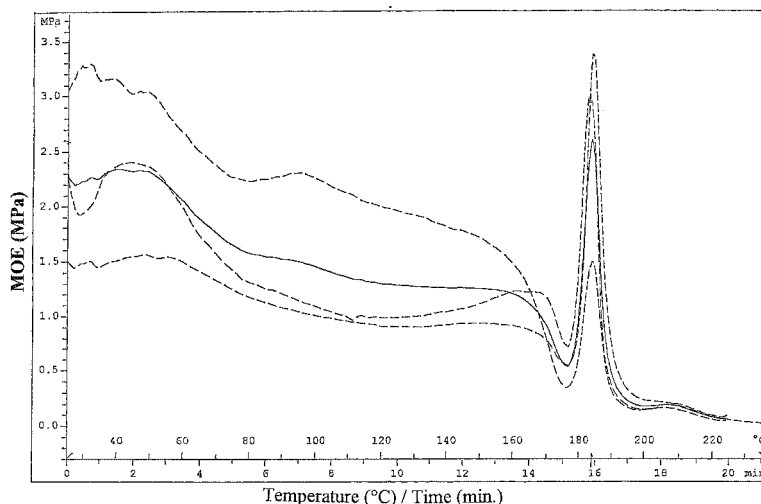
Figure 3 An example of type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of untanned pickled hide. Continuous curve is the averaged one.

tion of melamine, either (a) the higher is the shrinkage temperature or (b) the higher is the shrinkage temperature at lower proportions of melamine.

To again visualize at a glance what is the influence of certain parameters on the shrinkage temperature, curves of the increase of the shrinkage temperature as a function of the percentage of MUF resin are shown in Figures 1 and 2.

In Figures 1 and 2 and Table II are shown the main differences of the type of MUF formulation on the increase of shrinkage temperature for quebracho and mimosa tannins. It is interesting that leathers treated with either of the two tannins have at least one formulation presenting just about the same shrinkage temperature as the chrome treated control at only 25% MUF content, and several others that are very close to it. The two lower shrinkage-yielding formulations based on quebracho tannin have widely different MUF molar ratios (1.8 and 1.2) but the same M:U weight ratio (47:53), indicating that in quebracho the latter one might be the more important MUF parameter to control shrinkage temperature. In mimosa tannin treated leathers instead, 5 of the best 6 formulations have a high MUF molar ratio (three have 2.5 and two have 1.8), indicating that this is the most important parameter for this tannin in determining the shrinkage temperature. The M:U weight ratio appears to have much less influence in mimosa, with the 47:53 ratio being the one for half of the top 6 curves but 20:80 and 30:70 giving equally good performances. It again confirms that excellent combinations can be obtained for both tannins. Between the two mimosa tannin presents perhaps a greater ease of formulation and appears to yield leather of slightly better flexibility. This indicates that the mimosa tannin used is more

water resistant in the network and thus that the proportion of melamine is less important to final performance. Quebracho instead appears to be more water sensitive and it is then the proportion of water-resistant melamine in the formulation that is more important. This is logical as the quebracho used (Indusol Ato) is heavily sulfited (at the 10% level) and hence the finished network it forms is much more sensitive to water attack than a network based on a mimosa tannin only sulfited at the 1% level. It is not the tannin in itself that needs a MUF formulation or other, but the way the tannin used has been pretreated that determines which MUF one needs to use for optimal performance in antishrinkage effectiveness.

The interesting trend in Table II and in Figures 1 and 2 is the shape of the shrinkage temperature curves, all, with a very few exceptions, appearing to run almost asymptotically toward the value obtained for the chrome tanned wet-blue hide leather.

TMA of experimental leathers and an alternative method for the correlation of leathers shrinkage temperatures

TMA in tension of several of the samples of leather prepared was also carried out. This was done to determine a mathematical relationship connecting some of TMA-obtained parameters with the shrinkage temperature or other characteristics of the leather produced. It was also done to evaluate if TMA could give a deeper insight into the reaction processes that occur at the molecular level between tannin and hide in the preparation of leather. This approach was taken and explored, then, mainly with a view to develop different and more explicative methods of testing some of the fundamental parameters in leather making. It is,
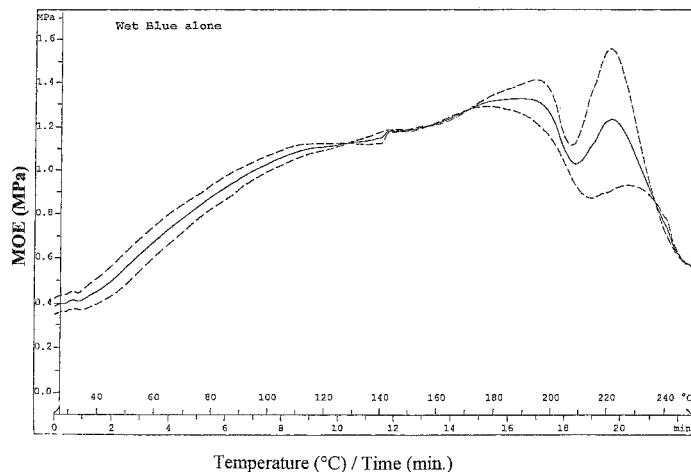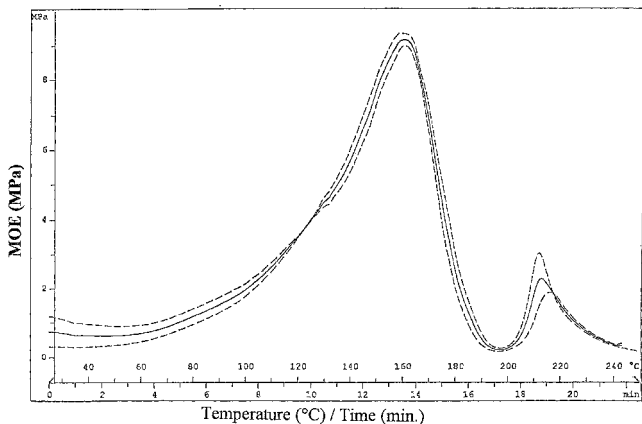
Figure 4 An example of type of curve obtained for variation of MOE as a function of temperature and time in TMA constant heating rate tension test of chrome tanned (4.8% chrome) wet-blue hide. Continuous curve is the averaged one.

however, important to discuss first the few results obtained for leather prepared with just pure vegetable tannins.

Examples of some TMA thermograms of MOE in tension as a function of temperature for a constant heating rate of 10°C/min shown in Figures 3–8 show that the pure vegetable materials all show two main thermogram peaks followed by a third one at much higher temperature. Lignosulfonate-produced leather, for instance, shows the first two peaks practically co-incidental (only a shoulder indicates the presence of the other peak, the appearance being mainly that of a huge single peak). Standard chestnut C produced leather shows the two peaks but very close one to the other and the two flavonoid tannins produced leather, both mimosa and quebracho, showing also two peaks but well separated and distinct one from the other. The relative intensity of the peaks and hence the MOE

values obtained and the temperature at which they occur are also of particular interest (Table III).

The results in Figures 5 and 6, and Table III, indicate that in the case of simpler phenolics as lignosulfonates and an hydrolyzable tannin as chestnut, the position and intensity of the first peak follows the efficiency of tanning. It appears to depend too from the flexibility of the leather. This is so on the basis that a stronger but less brittle material yields a high strength due to a much more efficient dispersion of the viscoelastic energy of the material. Thus, passing from an industrial lignosulfonate to chestnut one passes from the first peak small/second peak big, to the chestnut both peaks big situation. The MOE of chestnut tanned leather is also much higher than that of the lignosulfonate (which gives instead a hard, but brittle and inelastic, unsuitable material). This indicates that

Figure 5 An example of type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of lignosulfonate rigid leather. Continuous curve is the averaged one.
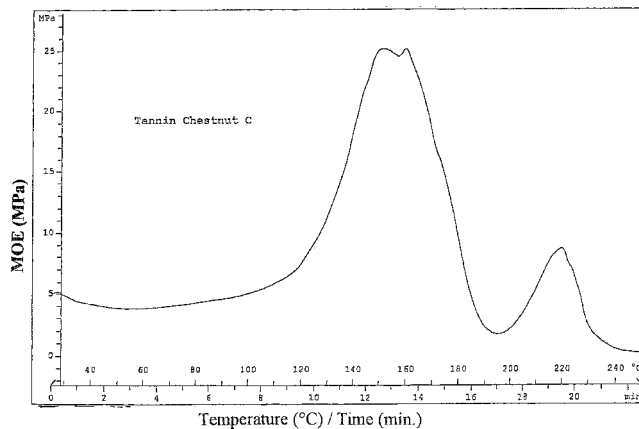
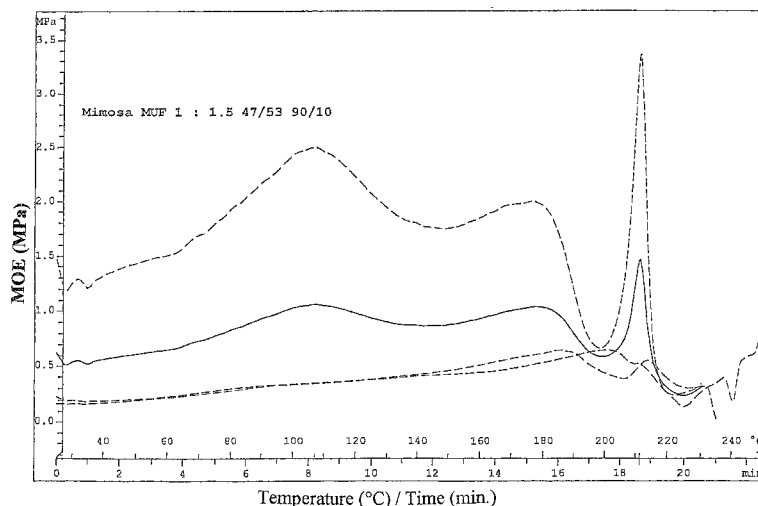

Figure 6 An example of type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of leather tanned only with chestnut tannin extract. Continuous curve is the averaged one.
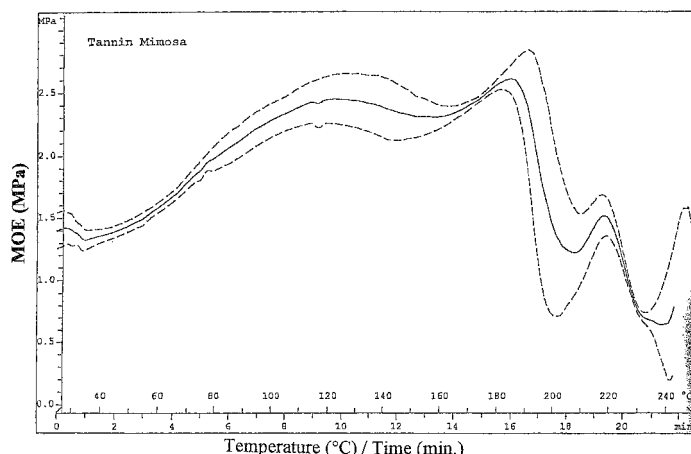
Figure 7 An example of type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of leather tanned only with mimosa tannin extract. Continuous curve is the averaged one.

chestnut tannin gives a much more flexible but also much stronger leather than lignosulfonate, which is indeed the case. It is, however, the lower temperature peak that has moved to higher temperature. Thus, three parameters are of importance to define what has occurred: the MOE value of the peak and the temperature at which the peak occurs. The higher these two parameters are, the more elastic, tougher, and stronger the leather. The third determining parameter appears to be the relative intensity of the first peak in relation to the second. The higher the MOE value of the first peak is in relation to the second, the better the leather. However, it has proved impossible to define well or to quantify this last effect with the data available. In lignosulfonates (Fig. 5), the first and second peak are much more apart than the TMA thermogram figure makes it appear at first sight.

The temperature of the maximum of the second peak does not appear to change much except for the chrome tanned leather. It should then be the temperature (but definitely not the intensity—if one looks at the low intensity observed in the wet-blue case) of the maximum MOE of the second peak that might then be related to the shrinkage temperature of the leather. Chrome tanned leather gives a much higher shrinkage temperature then vegetable tanned leather, and the temperature of the second TMA peak is distinguished by being much higher for chrome tanned leather (at 190°C against a value of around 155–168°C for the vegetable tan). According to this, one could forecast from Table III that quebracho and mimosa tanned leathers are stronger, heavier, and perhaps less flexible leathers than chrome tanned, but less strong and more flexible than chestnut tanned one, but they also have a

Figure 8 An example of type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of leather tanned with a MUF resin (1:1.5, 47:53) + mimosa tannin extract in weight proportion 10:90. Continuous curve is the averaged one.

TABLE III
TMA Leather Tension Test Peaks, Their Temperature, and Their Maximum MOE Value in Correlation with Shrinkage Temperature by Classical Method of Experimental Leathers Tanned with MUF/Vegetable Tannins

Formulation	Tannin/MUF (%)	First peak T (°C)	MOE (MPa)	Second peak T (°C)	MOE (MPa)	Third peak T (°C)	MOE (MPa)	Ave. temp. T (°C)	MOE ave. (MPa)	Shrink temp (°C)
Chestnut	90/10	93.3	0.92	189.6	1.15	236.6	0.49	173	0.85	77
C MUF 1:2.5 47/53	75/25	77.8	0.7	187.2	0.89	236.2	0.37	167	0.65	78
	50/50	105.87	0.94	182.23	0.99	208.4	0.78	166	0.90	79
Chestnut	90/10	102.5	2.01	168	1.69	232.8	0.6	168	1.43	67
C MUF 1:1.8 47/53	75/25	109.9	2.18	161	1.86	233.9	0.49	168	1.51	76
	50/50	111.45	2.73	166.2	2.33	216.1	0.66	165	1.91	87
Mimosa	90/10	113.15	4.89	161.4	3.65	181.1	0.91	152	3.15	89
MUF 1:2.5 47/53	75/25	117.5	4.04	177.1	3.41	222.9	0.29	173	2.58	90
	50/50	169.5	0.97	215.9	0.67	240.3	0.26	209	0.63	92
Mimosa	90/10	125.8	5.22	187.5	0.51	213.7	0.7	176	2.14	81
MUF 1:1.8 47/53	75/25	92.9	2.17	194.2	0.84	220.6	0.6	169	1.20	88
	50/50	121.7	0.7	192.2	0.79	240.2	0.39	185	0.63	92
Quebracho MUF 1:	90/10	121.3	0.5	204.4	1.62	236.8	0.2	188	0.77	81
1.8 47/53	75/25	142.1	0.42	203	1.03	237.3	0.23	194	0.56	89
	50/50	119.2	0.57	191.6	0.75	220.7	0.78	177	0.70	90
Quebracho MUF 1:	90/10	90.1	0.42	196.5	0.73	223.4	0.31	170	0.49	79
2.5 47/53	75/25	99.2	0.58	206.7	1.94	238.5	0.28	181	0.93	86
	50/50	177.02	0.79	213.2	1.4	235	0.29	208	0.83	89
Chestnut	90/10	123.3	1.27	197.4	1.49	221.8	0.96	181	1.24	72
C MUF 1:1.8 30/70	75/25	110	0.66	195.8	0.92	224.16	0.54	177	0.71	73
	50/50	103.3	1.15	178.8	1.25	203.6	1.02	162	1.14	75
Mimosa	90/10	118.2	0.64	181.1	0.84	222.5	0.43	174	0.64	77
MUF 1:1.8 30/70	75/25	118.95	0.46	194.99	0.82	225.8	0.39	180	0.56	84
	50/50	102.3	1.02	193.7	0.28	226.7	0.25	174	0.62	87
Quebracho MUF 1:	90/10	122.32	0.66	207.32	1.15	244.75	0.4	191	0.74	80
1.8 30/70	75/25	102.88	3.56	172.2	1.97	222.8	0.88	166	2.14	83
	50/50	77.53	5.41	122.8	5.79	195.4	0.81	132	4.00	86
Mimosa	90/10	112.1	0.62	196.7	0.91	222.9	1	177	0.84	76
MUF 1:2.5 20/80	75/25	102.8	0.61	190.5	1.15	220.1	1.1	171	0.95	91
	50/50	87.1	0.72	185.8	1.04	213	0.91	162	0.89	92
Chestnut	90/10	96.72	0.53	206.96	1.01	236	0.91	180	0.82	69
C MUF 1:2.5 20/80	75/25	110.65	0.53	198.08	0.91	229.07	1.22	179	0.89	71
	50/50	96.2	0.73	189.5	0.87	224.4	0.95	170	0.85	75
Quebracho MUF 1:	90/10	129.6	0.98	206	1.13	229.2	0.4	188	0.84	81
1.5 47/53	75/25	143.8	0.69	183.5	0.95	210.8	1.97	179	1.20	83
	50/50	144.6	0.58	193.1	0.66	232.5	0.29	190	0.51	86
Quebracho MUF 1:	90/10	115.73	0.65	202.2	1.92	232.9	0.26	184	0.94	81
2.5 20/80	75/25	127.92	0.59	202.2	2.1	235.3	0.26	188	0.98	82
pH5	50/50	180.47	0.95	211.6	0.97	232.7	0.26	208	0.73	83
Quebracho MUF 1:	90/10	108.2	1.92	173.6	2.38	210	2.75	164	2.35	83
2.5 30/70	75/25	110.1	1.65	174.7	1.56	216.1	1.38	167	1.73	83.5
	50/50	111.8	5.35	176.4	2	220	1.57	169	2.97	84
Mimosa	90/10	90.25	0.54	201.4	0.77	216.4	0.62	169	0.64	83
MUF 1:2.5 30/70	75/25	77.7	0.61	138.2	0.78	195.1	0.94	137	0.78	87
	50/50	109.17	1.03	186	1.28	209.8	1.98	168	1.43	89
Chestnut	90/10	113.41	0.58	190.45	0.95	223.7	1.64	176	1.06	71
C MUF 1:2.5 30/70	75/25	117.42	0.65	176.27	0.94	223.6	1.74	172	1.11	73
	50/50	93.07	1.4	160.26	1.22	212.95	1.27	155	1.30	78
Quebracho MUF 1:	90/10	108.17	0.63	197.9	1.19	210.2	1.7	172	1.17	81
1.8 20/80	75/25	104.5	0.55	193.1	1.01	212.75	2.03	170	1.20	85
	50/50	102.5	0.84	188.8	1.2	208.8	1.73	167	1.26	87
Chestnut	90/10	125.77	0.71	193.21	1.1	225.13	2.31	161	1.37	70
C MUF 1:1.8 20/80	75/25	101.8	0.97	189.06	1.17	208.8	1.64	167	1.26	75
	50/50	95.78	0.84	182.47	0.97	220.65	1.1	166	0.97	76
Mimosa	90/10	137.41	0.8	192.03	1.15	210.6	0.9	180	0.95	80
MUF 1:1.8 20/80	75/25	95.73	0.97	186.43	1.22	213.75	1.67	165	1.29	88
	50/50	62.21	10.59	104.86	7.45	195.36	0.95	121	6.33	90
Mimosa	90/10	75.96	2.69	176.99	1.55	208.44	0.58	154	1.61	86
MUF 1:1.2 47/53	75/25	75.86	1.26	176.32	1.55	213.65	3.53	155	2.11	86
	50/50	71.18	3.81	120.47	3.51	218.25	0.76	137	2.69	86
Quebracho MUF 1:	90/10	115.54	0.74	187.8	1.06	210.85	0.93	171	0.91	79
1.2 47/53	75/25	113.1	0.66	187.8	1	206	1.25	169	0.97	91
	50/50	105.1	0.74	182.9	0.88	215.4	0.54	168	0.72	92
Chestnut	90/10	116.87	0.49	170.35	1.56	228.63	0.34	172	0.80	75
C MUF 1:1.2 47/53	75/25	102.91	0.88	189.94	1.15	212.3	1.06	168	1.03	75
	50/50	92.58	0.42	191.56	0.71	22.97	0.27	102	0.47	75

much lower shrinkage temperature than the chrome tanned one. This is indeed the case, proving already that a TMA approach can yield quickly scanning information on different leathers.

The third peak at much higher temperature appears instead to be something characteristic of the hide, but the intensity of which gets enhanced both in absolute and in proportion to the other two peaks, by the

tanning of the material. This last peak is due to the degradation of the hide as can be seen from the burned-out appearance of the sample immediately after its occurrence and the burned smell of the sample after this final peak. It is then a peak marking the ultimate degradation of the leather sample and the increase in MOE might well correspond to a series of happenings such as the elimination of the last water tightly bound to the collagen at molecular level, and to degradative internal wet and dry rearrangements that follow the initial coagulation marked by peak number two.

On the above generalized response of the natural tannins, the additional introduction of MUF resins of markedly different formulations yields a further variation of results, a variation of results that is well in line with what has been found by other techniques. Thus, for the flavonoid tannins the larger average dimensions of the molecule of quebracho due to the higher average degree of polymerization of this tannin somewhat slows down or partly inhibits the penetration of the tanning solution into the hide and as a consequence a lower retention load of tannin in the final leather is the likely result. This appears also to be the only reason why quebracho tannin-based formulations tend to always have slightly lower shrinkage temperatures than mimosa tannin-based ones. It means that quebracho may give even better results once its penetration ability is improved.

At acid pH the tendency appears to be that as the MUF proportion decreases the TMA measured MOE of the leather increases. The MOE peaks are a direct measure of resistance of the leather to the contraction force exercised in tension on the sample at both the shrinkage temperature and at other temperatures. This means that the lower the value of the MOE, the worse are the antishrinkage properties of the leather. This means that the treatment has improved the resistance to the contraction force by some molecular level rearrangement due to the treatment, be this crosslinking or viscoelastic dissipation of stress. The trend appears to be that the TMA measured MOE of the leather decreases as the MUF proportion decreases. Thus, the leather is poorer the lower the MUF proportion. This is possibly due to the decrease of crosslinking engendered by the lower amount of MUF resin, both possibly on the hide and on the tannin. This behavior is due to the difference in reactivity of the two systems at the given pH because of the following:

1. The reactivity of the tannin with any HCHO source, including MUF resins, is relatively lower at the tanning pH (pH 5 was used here)
2. The reactivity of the MUF resin with itself is instead relatively greater at pH 5

At pH 5 the MUF has, then, a predominant tendency here to react with itself. A higher proportion of MUF,

such as in tannin/MUF 50/50, will statistically favor reaction of some portion of the MUF with the tannin. The tannin is forced, then, to coreact more extensively with the MUF while the MUF still also reacts with itself, with the tannin attached (tanning) by secondary forces to the hide collagen. As a consequence, two separate networks are formed in the tanning hide/leather, namely

- one formed by the autocondensation of the MUF resin alone (as extensive coreaction in heterogeneous phase on the amidic groups of the collagen does not appear likely to occur to any great extent, if any at all);
- one, here likely to be in higher proportion but not possibly the major pattern, formed by the coreaction of the flavonoid tannin with the MUF.

The TMA measured coagulation MOE of the leather formed is lower than what could be as there is synergy between the two materials: The tannin tans and the MUF reinforces it in the copolymerization network, with the MUF only network interpenetrating the tannin/MUF one and still contributing to stiffness, body, mechanical resistance, and antishrinkage characteristics of the leather.

If instead we decrease the proportion of MUF, the MUF resin, although possibly more completely reacted with the excess of tannin, is in smaller proportion in the copolymerization network with the tannin. In such an eventuality there is less MUF to help crosslinking to contribute to leather stability. At such a lower absolute amount of MUF even a much greater proportion of MUF resin might have reacted with itself, although this is not sure. The tannin can tan (adhere to) the collagen by secondary forces carrying in the same network only a minor part of the MUF. A set of mostly separate interpenetrating networks is formed. These are (1) the now weaker tannin one copolymerized with a small proportion of MUF, the only tanning network present but now weaker due to the low proportion of MUF; and (2) the separate, smaller MUF network, which does not tan the leather. The combination of all this yields a leather of much lower strength and much poorer antishrinkage capability.

The temperature at which the TMA thermogram peaks appear is influenced by the same relative balance of the two interpenetrating networks discussed above. Thus, the higher the antishrinkage capability—the higher is the shrinkage temperature—the lower is the MOE of the leather. The higher the temperature at which a certain peak appears, the more resistance to shrinkage does the leather possess. Equally, the longer the time, at constant heating rate, before a certain peak appears the more resistance to shrinkage does the leather possess. Thus, and this is particularly notice-
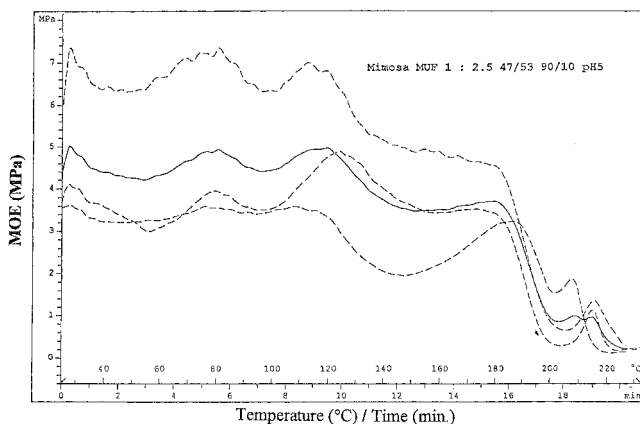
Figure 9 A rare example of the type of curve obtained for the variation of MOE as a function of temperature and time in TMA constant heating rate tension test of leather tanned with a MUF resin (1:1.5, 47:53) + mimosa tannin extract in weight proportion 10:90, in which all the five peaks also visible in untanned pickled hide are still visible. Continuous curve is the averaged one.

able for quebracho tannin, the higher the proportion of MUF, the higher is the relative proportion of the tannin/MUF copolymerized network. The higher the relative proportion of the tannin/MUF copolymerized network, the higher/better is the leather shrinkage temperature measured by classical means. The higher the leather shrinkage temperature, the higher is the temperature at which the TMA MOE peaks are shifted. This is indeed the case, as can be seen from Table III.

To conclude, then, for highly formaldehyde and formaldehyde–resins–reactive polyflavonoid tannins, the TMA in tension of the leather indicates improved antishrinkage performance the higher is the values of

the TMA's MOE and the higher is the temperatures at which the MOE maximum peaks appear.

In the case of chestnut tannin, an hydrolyzable ellagitannin, one can notice that the MUF resin prefers to react with itself rather than with the tannin, this tannin reactivity and rate of reaction with any formaldehyde source being much slower than for the flavonoid tannins. We will then tend to have mainly a pure MUF network independent of the almost pure tannin network with traces of MUF that tans the hide, and consequently the shrinkage of the leather produced will be worse. The notable exception, chestnut/MUF(1.8, 47:53,50/50), indicates that a narrow window of conditions does, however, exist in which a real improvement can still be obtained. This behavior is then the consequence of the well-known much lower reactivity toward methylol groups of the phenolic nuclei of hydrolyzable tannins in relation to the flavonoid ones.[4] With chestnut tannin the TMA indications are that the use of a MUF of lower molar ratio, thus 1.8 allows to obtain a higher MOE, which indeed corresponds to the shrinkage temperature results in Table III and to the best chestnut formulation found by classical shrinkage temperature testing. It must be noticed, however, that excluding this chestnut formulation, the shrinkage temperatures for chestnut-based formulations are consistently and considerably much lower than for the flavonoid tannin formulations. This is reflected in the TMA results (see Table III) by the lower MOE maximum peak temperatures and higher MOE peak values when chestnut is the tannin in the formulation.

This behavior is just schematically exemplified by the trends of the maximum MOE value indicating why in certain intervals the type and amount of MUF
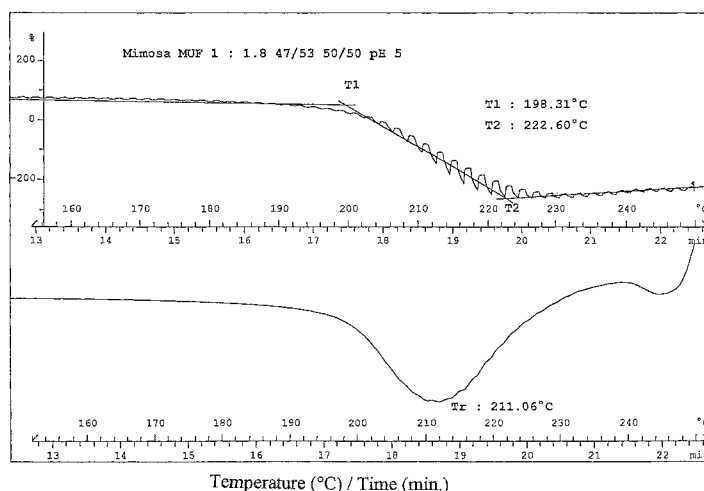
Figure 10 An example of type of curve obtained for percentage shrinkage vs temperature and time in TMA constant heating rate tension test (according to the approach in ref. 10) of leather tanned with a MUF resin (1:1.8, 47:53) + mimosa tannin extract in weight proportion 50:50 (top curve) indicating T_1 and T_2. The bottom curve is its first derivative and the peak indicates the value of T_r.

TABLE IV
TMA Leather Compression Test T_1, T_2, and T_r Temperatures of Experimental
Leathers Tanned with MUF/Vegetable Tannis

Formulation	T_1 (°C)	T_2 (°C)	T_r (°C)	Shrinkage T (°C)
Chestnut C MUF 1:2.5 47/53 pH 5	197	219	210	77
	195	224	209	78
	183	199	192	79
Chestnut C MUF 1:1.8 47/53 pH 5	193	216	205	67
	189	208	200	76
	185	200	193	87
Mimosa MUF 1:2.5 47/53 pH 5	198	223	208	89
	192	202	198	90
	190	225	210	92
Mimosa MUF 1:1.8 47/53 pH 5	202	217	211	81
	197	225	212	88
	198	226	214	92
Quebracho MUF 1:1.8 47/53 pH 5	193	224	214	81
	192	225	212	89
	189	222	199	90
Quebracho MUF 1:2.5 47/53 pH 5	202	224	213	79
	198	225	215	86
	185	226	198	89
Chestnut C MUF 1:1.8 30/70 pH 5	196	231	211	72
	197	230	214	73
	186	222	197	75
Mimosa MUF 1:1.8 30/70 pH 5	194	218	204	77
	191	225	210	84
	183	211	197	87
Quebracho MUF 1:1.8 30/70 pH 5	212	235	224	80
	219	237	226	83
	222	239	232	86
Mimosa MUF 1:2.5 20/80 pH 5	203	236	225	76
	198	233	220	91
	187	231	201	92
Chestnut C MUF 1:2.5 20/80 pH 5	204	238	222	69
	200	237	216	71
	194	229	203	75
Quebracho MUF 1:1.5 47/53 pH 5	198	225	209	81
	192	223	207	83
	198	221	209	86
Quebracho MUF 1:2.5 20/80 pH 5	193	226	209	81
	192	221	212	82
	186	224	202	83
Quebracho MUF 1:2.5 30/70 pH 5	189	227	213	83
	188	232	221	83, 5
	189	230	197	84
Mimosa MUF 1:2.5 30/70 pH 5	204	222	213	83
	199	219	210	87
	190	229	200	89
Chestnut C MUF 1:2.5 30/70 pH 5	195	235	214	71
	197	235	215	73
	186	222	194	78
Quebracho MUF 1:1.8 20/80 pH 5	201	232	213	81
	197	230	220	85
	201	233	219	87
Chestnut C MUF 1:1.8 20/80 pH 5	194	244	213	70
	197	230	211	75
	192	233	205	76
Mimosa MUF 1:1.8 20/80 pH 5	199	224	213	80
	194	223	204	88
	173	199	181	90
Mimosa MUF 1:1.2 47/53 pH 5	183	199	192	86
	189	212	198	86
	185	215	207	86
Quebracho MUF 1:1.2 47/53 pH 5	195	218	205	79
	195	218	209	91
	197	220	211	92
Chestnut C MUF 1:1.2 47/53 pH 5	200	230	221	75
	193	228	210	75
	193	224	207	75

TABLE V
Type of Regressions Tried to Correlate Classical Shrinkage Temperature with the Temperatures T_1, T_2, and T_3 and MOE_1, MOE_2, and MOE_3 Obtained by TMA in Tension

$$T_{\text{shrinkage}} = A\, T_{\text{peak 1}} + B\, T_{\text{peak 2}} + C\, T_{\text{peak 3}}$$
$$T_{\text{shrinkage}} = A\, \text{MOE}_{\text{peak 1}} + B\, \text{MOE}_{\text{peak 2}} + C\, \text{MOE}_{\text{peak 3}}$$
$$T_{\text{shrinkage}} = A\, T_{\text{average TMA}} + B\, \text{MOE}_{\text{average TMA}}$$
$$T_{\text{shrinkage}} = A\, T_{\text{peak 1}} * \text{MOE}_{\text{peak 1}} + B\, T_{\text{peak 2}} * \text{MOE}_{\text{peak 2}} + C\, T_{\text{peak 3}} * \text{MOE}_{\text{peak 3}}$$
$$T_{\text{shrinkage}} = A\, T_{\text{peak 1}} + B\, \text{MOE}_{\text{peak 1}} + C\, T_{\text{peak 2}} + D\, \text{MOE}_{\text{peak 2}} + E\, T_{\text{peak 3}} + F\, \text{MOE}_{\text{peak 3}}$$

resin used need to be changed to obtain maximum effect.

One peculiarity that can be noted in the thermogram of pickled, untanned hide in Figure 3 is the existence of two minor peaks other than those observed in the different tanned leathers. These are the peaks at 40–50°C and the small one at 210°C. The low temperature peak is definitely due to the loss of excess low energy bound water characteristic of pickled hides, which are much wetter than tanned hides. In the thermograms 4–8 of tanned leathers the peak at low temperatures has disappeared because the equilibrium moisture content of a tanned hide, as wet as tested, is still much lower than that of pickled hide. All the other peaks (the main three peaks) do shift at higher temperatures in tanned hides: it is then the very pronounced pickled hide peak at 190°C that shifts to 210–220°C as one tans the hide (Figs. 4–8) that masks in tanned leathers the very small peak at 210°C in Figure 3. However, in some rare cases also in tanned leather it is possible to observe all five peaks. This occurs with higher frequency where MUF resin with a high content of formaldehyde have been used, hence with a (M+U):F 1:2.5 ratio. An example of this is shown in the thermogram of Figure 9 of a leather obtained by tanning with mimosa tannin/MUF (1:2.5, 47/53) in the proportion 90/10 where five peaks at 30, 80, 120, 180, and 210–220°C are observed (the split of the 210–220°C peak in two peaks in the averaged continuous curve in Figure 9 is only an artifact of the averaging of the three curves obtained).

TMA Correlation with leathers shrinkage temperatures

As regards a method to develop an algorithm to compare mathematically the antishrinkage effectiveness of leathers with the results of the TMA, two different approaches were taken: (1) Correlation of the leather shrinkage temperature with the temperatures and MOE values of the three peaks observed in TMA tests in tension (Table III). (2) Correlation of the leather shrinkage temperature with the leather glass transition temperature and with the initial and final temperatures limiting the leather viscoelastic transition obtained by TMA tests in compression according to a method already proposed by other authors[10] (Table IV).

In the first approach, the three parameters that appear to count follow:

1. The average of the temperatures at which the three TMA peaks occur: the higher this is, the better is the leather as regards antishrinkage effectiveness.
2. The average of maximum MOE values of the TMA peaks: the higher this average is, the better is the leather as regards antishrinkage effectiveness. This means the MOE is a measure of the resistance to the contraction force induced by heat and temperature.
3. The relative intensity of the first TMA peak in relation to the second: the higher is the first in proportion to the second, the better appearing the leather sometimes is. However, it has not been possible to better define or quantify such an effect.

Several correlation algorithms were tried for all the samples indicated in Tables II and III. These are indicated in Table V. Of these, only one gave very good results, namely,

$$\text{classical } T_{\text{shrinkage}} = A\, T_{\text{average TMA}} + B\, \text{MOE}_{\text{average TMA}}$$

where the coefficients A and B are shown in Table VI for the cases in which eq. (1) is applied to all cases in Table II, or just to all the chestnut tannin case, or to just the mimosa tannin cases, or to just the quebracho tannin cases. The other algorithms tried (Table V) gave considerably worse calculated errors—to the point that in most (but not in all cases) the results of these expressions were not significant. Often the error was relatively small for one of the variables [but always higher than what obtained with eq. (1)] but extremely high for the others, and this did not apply always to the same variables in all the cases. The values of each single peak appear to correlate somewhat, but not really well, and not really unambiguously (with some rare exceptions) with the shrinkage temperature obtained by classical means, indicating that the transitions corresponding to each peak are all three related to and involved with leather shrinkage. It is then clear that each peak is likely to describe the same transition but for the same material in a different physical state.

TABLE VI
Best Correlation Equation, Its Coefficients, Standard Deviations, and Errors for the Correlation
of Experimental Leather Shrinkage Temperatures Obtained by Classical Method and TMA Leather
Tension Test Average Peak Temperature and the Average of Their Maximum MOE Values

Best model tried: classical $T_{\text{shrinkage}} = A\ T_{\text{average TMA}} + B\ \text{MOE}_{\text{average TMA}}$
Average temperature and average MOE model calculated on all values and all tannins
A: 4.2656832×10^{-1} (SD: 8.87×10^{-3}) (error 2%)
B: 6.5551107 (SD: 9.67×10^{-1}) (error 15%)
Average temperature and average MOE model calculated only on chestnut values
A: 3.9556758×10^{-1} (SD: 2.597×10^{-2}) (error 7%)
B: 6.5697588 (SD: 3.997) (error 61%)
Average temperature and average MOE model calculated only on mimosa values
A: 4.6469259×10^{-1} (SD: 1.467×10^{-2}) (error 3%)
B: 5.6507274 (SD: 1.206) (error 21%)
Average temperature and average MOE model calculated only on quebracho values
A: 4.2960623×10^{-1} (SD: 1.229×10^{-2}) (error 3%)
B: 6.3182619 (SD: 1.483) (error 23%)

Thus, one of the peaks is likely to correspond to the glass transition of leather or of the entangled main body chains of collagen, a second peak is most likely to correspond to the secondary transition due to the collagens chain ends describing crank-handle movements, and the third corresponds to the movement and rearrangement of microcrystalline or ordered collagen structures, this transition being possibly the higher temperature peak of the three. The relative contribution of the parameters in each peak indicate that logically the T_g transition is likely to be the one represented from the first or second peak, but the lack of consistent correlation with all cases impede us to assert categorically that this is the case and which of the two peaks is the one that best represents it. It is clear from this that one deals here with a series of very complex interactions that are not readily quantified, understood, or even correlated with what really occurs at the molecular level. However, the two easier and quantitatively measurable parameters—namely, the average of the MOE values at the three maximum peak temperatures and the average of the three maximum temperatures of the three peaks, hence averaged over all the three TMA peaks—appear to be readily combined and to correlate well with the shrinkage temperature measured by traditional testing methods through eq. (1).

The second approach using TMA tests in tension but according to a different method[10] (Fig. 10) was based on a raw TMA curve of percentage shrinkage as a function of temperature where the interval considered is the T_g region comprised between a temperature T_1 and T_2—namely, the extrapolated onset and end temperatures of the T_g region—and the third parameter is the temperature T_r defining the temperature of maximum rate of relaxation, corresponding to the peak of the first derivative of the curve in Figure 10. This approach was also able to yield a predictive equation:

$$\text{classical } T_{\text{shrinkage}} = AT_1 + BT_2$$

but this was valid exclusively for the chestnut tannin case (Table VII) and even in this best of cases gave calculated percentage errors that were much higher than in all the cases of eq. (1) (Table VII). Thus, while the method that has led to eq. (1), and eq. (1) itself, have good predictive value, eq. (2) and the TMA test method leading to it are far too limited to forecast the leather shrinkage temperature. The other possible predictive correlation equation tried for method 2 (Table VIII) gave even worse results.

CONCLUSIONS

An experimental sulfonated MUF resin of relatively low melamine content, prepared according to a basic sequential formulation used for wood gluing, has been shown to be highly effective when coupled with different natural vegetable tannins to produce leather with the same good characteristics of leather prepared with chrome salts. In particular, the antishrinkage effectiveness of the leather prepared according to the new approach is comparable to that obtained with chrome tanned leathers. The comparison of the traditional leather shrinkage temperatures test method with a new TMA test method in tension has yielded a mathematical relationship correlating the thermogram peak temperatures and MOE averages with the traditional shrinkage temperature to a high degree of confidence. A previous TMA test method, in compression, has proven to yield more problematic and finally not very reliable results when one needs to apply it to a wide variety of different cases.

TABLE VII
Type of Regressions Tried to Correlate Classical
Shrinkage Temperature with the Temperatures T_1, T_2
and T_r Obtained by TMA in Compression Model

$T_{\text{shrinkage}} = A\ T_1 + B\ T_2 + C\ T_r$
$T_{\text{shrinkage}} = A\ T_1 + B\ T_2$

TABLE VIII
Best Correlation Equation, Its Coefficients, Standard Deviations, and Errors for the Correlation
of Experimental Leather Shrinkage Temperatures Obtained by Classical Method
and TMA Leather Compression Test temperatures T_1 and T_2

classical $T_{\text{shrinkage}} = A\,T_1 + B\,T_2$
Average glass transition temperature model adapted to deflection approach and calculated only on chestnut values
A: 7.1417269 E − 1 (SD: 1.611 E − 1) (error 23%)
B: − 2.8326360 E − 1 (SD: 1.384 E − 1) (error 49%)

References

1. International Norm, International Leather Union I.U.C./18, Determination of the leather content of Cr[VI], 1995.
2. European Union Directives 91/271/Cee and 91/676/Cee on water effluents, 1999.
3. Noferi, M.; Masson, E.; Merlin, A.; Pizzi, A; Deglise, X. J Appl Polym Sci 1997, 63, 475–482.
4. Pizzi, A. In Wood Adhesives Chemistry and Technology; Pizzi, A., Ed.; Marcel Dekker: New York, 1983.
5. Marutzky, R. In Wood Adhesives Chemistry and Technology; Pizzi, A., Ed.; Marcel Dekker: New York, 1989; Vol 2.
6. Pizzi, A. Advanced Wood Adhesives Technology; Marcel Dekker: New York, 1994.
7. Pizzi, A.; Simon, C.; George, B.; Trosa, A. European Commission Contract Project QoL-99-00913, 2000–2003.
8. Naimark, W. A.; Waldman, S. D.; Anderson, R. J.; Suzuki, B.; Pereira, C. A.; Lee, M. J. Biorheology 1998, 35(1), 1–16.
9. Smirnova, N. A.; Perepelkin, K. E.; Koitova, Z. Y.; Yudina, L. P. izv vyssh Uchebn Zaved Prom-sti 1998, 5, 115–116.
10. Bosch, T.; Manich, A. M.; Carilla, J.; Palop, R.; Cot, J. J Appl Polym Sci 2001, 82, 314.
11. Mercer, A.; Pizzi, A. Holzforschung Holzverwertung 1994, 46, 51–54.
12. Panamgama, L. A.; Pizzi, A. J Appl Polym Sci 1996, 59, 2055–2068.
13. Pizzi, A.; Panamgama, L. A. J Appl Polym Sci 1995, 58, 277–281.
14. Mercer, A. T.; Pizzi, A. J Appl Polym Sci 1996, 61, 1687–1696.
15. Mercer, A. T.; Pizzi, A. J Appl Polym Sci 1996, 61, 1697–1702.
16. Prestifilippo, M.; Pizzi, A.; Norback, H.; Lavisci, P. Holz Roh Werkstoff 1996, 54(6), 393–398.
17. Properzi, M.; Pizzi, A.; Uzielli, L. Holz Roh Werkstoff 2001, 59(6), 413–421.
18. Silva Chimica S. A. Private communications, 2000–2001.
19. Asystant, Asyst Software Technologies, Inc., Version 1.10, 1988.
20. Leather International Norm I.U.P./16, Measurement of the contraction temperature (T_g).
21. Simon, C. Ph.D. thesis, University of Nancy 1, Epinal, France 2002.