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## A NOVEL PROCESS FOR CONVERTING HIDES OR SCRAP LEATHER TO A NEW THERMOPLASTIC MATERIAL

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## EXECUTIVE SUMMARY

This project deals with the characterization and development of a new material, thermoplastic leather--PLEATHER--for which the raw material is abundantly available scrap from hides and leather. We found that important mechanical properties of PLEATHER are related to production parameters such as pressure and temperature. Advanced research methods are being used to gain insight into the internal structure to explain the behavior of PLEATHER. This permits the determination of the optimum parameters for making useful products by relatively simple production techniques (see fig. 3, page 10A).

At the University of Porto in Portugal, a scientific group has been established, as a result of this project, for research in fibers of natural origin, which may be in the form of scrap. The group is serving the leather industry in the region around Porto and forms an example of successful organization of scientific research in the service of local industry. This group has committed itself to helping, together with Israel, in the A.I.D. associated scientific development of Cameroon.

To date this project has generated eight publications in scientific and industrial journals, which have been read, cited and even copied in developing countries, according to the reactions we have received from researchers.

Research institutes from developed countries are especially interested in the ecological aspects of our research because of the need to dispose of the harmful scrap of chrome tanned leather that accumulate at various production stages.

RESEARCH OBJECTIVES:

The objective of this project is to help developing countries use their cheap indigenous raw materials for making useful products with high added value, for their own use or for export.

For this purpose a novel process has been developed to make a thermoplastic material from leather and hide scrap in a relatively simple way.

To characterize the new material mechanically, chemically and structurally a range of modern research methods are used.

Furthermore, the dechromizing of chrome tanned leather is investigated to help avoid ecological hazards of the scrap, a problem in need of a solution in developing and developed countries alike.

Portugal's Tanners Association and the University of Porto supported the research and the establishment of a group for natural fiber (and) materials research.

Israel supported a preliminary investigation for the use of thermoplastic leather, made from leather scrap, for packaging material.

## 5. METHODS AND RESULTS

Note: Publications number 1-5 and number 7 are an integral part of this section.

### 5.1 Production of samples of PLEATHER:

To obtain well-defined samples, the production of all the samples was initially done in Israel. Portugal then made its own samples for investigation.

Several grinders were tried for the grinding of pieces of leather and hide scrap. A commercially available Wiley grinder was used for commutating the leather in fibers, and a coffee grinder was

employed for transforming the fibers into fine powder. Both fibers and powder are used as raw material for the samples. The length of the fibers is about 5 mm, and the powder resembles coarse flour.

The influence of the fiber length on the strength of hot pressed leather was established. The hardness of samples made with 5 mm long fibers is four points higher on the shore D scale than the hardness of samples made with 1 mm long fibers (ref. 1).

5.2 Characterization of PLEATHER

The investigation of mechanical properties (hardness, compression strength, toughness measurements) as a function of process parameters and additives was done in Israel. Concurrently Portugal determined the internal structure by Scanning Electron Microscopy and biochemical methods.

5.2.1 Publication number 1 elaborates on the influence of additives on the hardness of PLEATHER. The compression strength of "pure" PLEATHER as a function of the production temperature at a constant pressure is given in Fig. 1 (measurement with a Hounsfield electric driven tensile machine). The internal structure of leather compared to PLEATHER samples produced at various temperatures and pressure can be seen in the Scanning Electron Micrographs of Fig. 2. A simple model and the factors leading to the production of the various structures are extensively discussed in publications number 2, 3, 4.

5.2.2 The molecular weight of PLEATHER was determined with gel electrophoresis and gel permeation chromatography. Gel electrophoresis proved to be not a very good technique for PLEATHER, a) because the support material had to be "opened up," and some resolution was lost;

and b) because the collagen fragments in PLEATHER do not have well defined molecular weights. Nevertheless, the results support a continuous range of molecular weights centered around 50/60 kDa. No specific bands were obtained in the range 10 to 400 kDa, thus indicating a random molecular weight distribution.

The results obtained with gel permeation chromatography were much more interesting. The chromatograms obtained by HPLC show defined zones with molecular weights of: a) ca. 1400 kDa spreading down to 50 kDa and b) a very clear zone in the range 30 to 10 kDa. All these results show that the tranformation leather-->PLEATHER takes place with extensive breakdown of the collagen structure and that a reasonable correlation exists between the processing conditions and the extension of collagen degradation (publication number 7).

## 5.3 Production Techniques for PLEATHER

These were done on a laboratory scale in Israel. Research on techniques for the dechromizing of chrome tanned leather was performed in Portugal.

5.3.1 Production techniques for PLEATHER were tried out on a lab scale. We worked mainly with Compression Molding Techniques. Injection molding has so far not been successful. Transfer molding did work. Boxes made by Compression Molding are shown in Fig. 3.

We performed viscosity tests, MFI (Melt Flow Index), with various grades of PLEATHER. A reasonable correlation exists between the processing conditions, the degree of collagen degradation as measured according to section 5.2.2, and the viscosity of PLEATHER. The higher the processing temperature, the smaller the molecular weight of the fibers, the lower the viscosity and the better the fluidity.

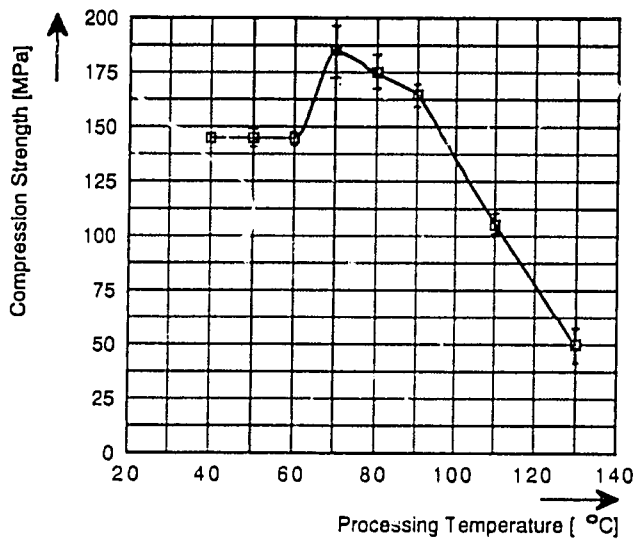
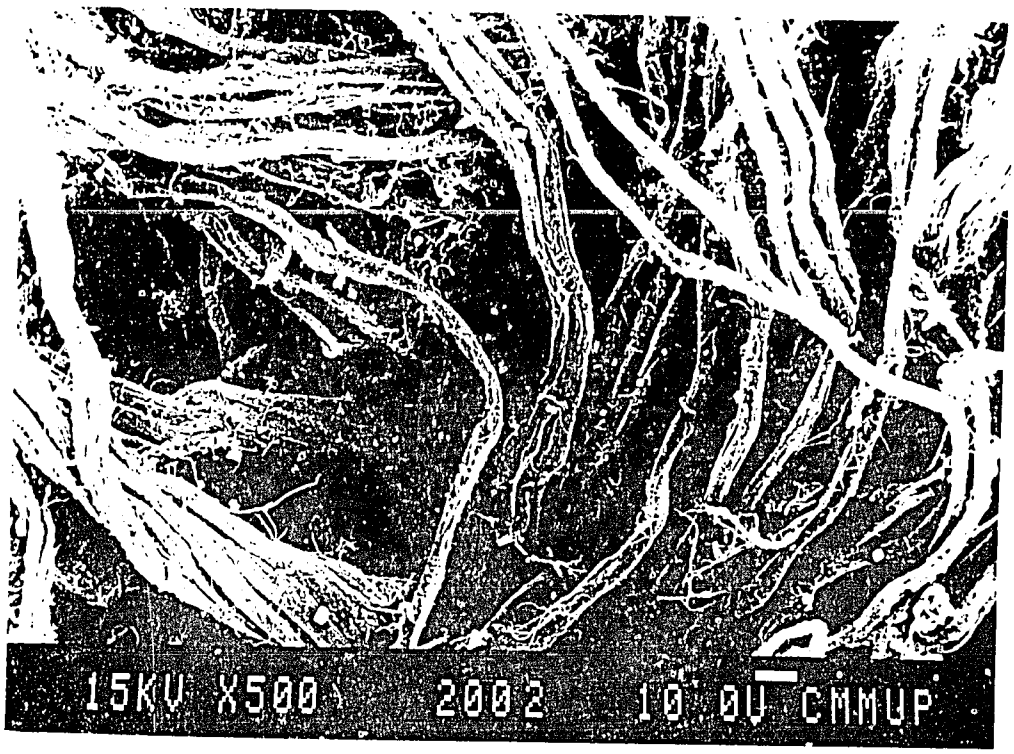



Fig. 1 Compression strength of thermoplastic leather measured as a function of processing temperature.

Processing Pressure = 650 bar.

Processing time = 6 min.

Each bar gives the spread in 5 measurements.




Scanning Electron Micrographs

Fig. 2a Internal Structure of Leather

Fiber bundles - 5-10 μm

Primitive fibers - ~ 1μm

Fibrils - ~ 0.1 μm

The white bar represents 10 μm.

Fig. 2b Continuous PLEATHER material with left-over Elastine fibers

Processing parameters: Pressure = 50 bar

Temperature = 155°C

Time = 6 min.

White bar = 10 μm

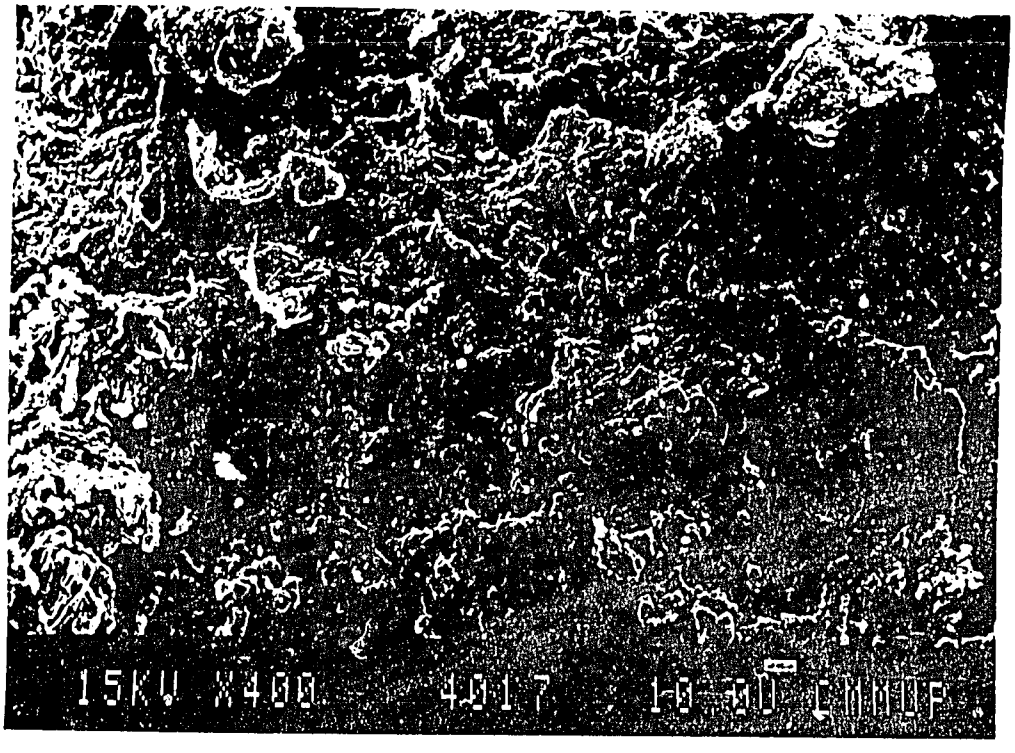



Fig. 2c Leaflike PLEATHER

Processing Parameters: P = 450 bar

T = 135°C

t = 6 min.

White bar = 10 μm

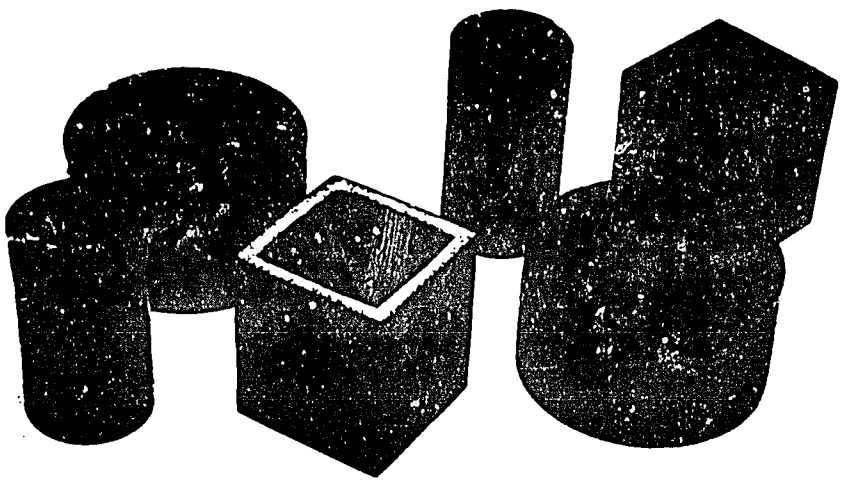


Fig. 3. Boxes made of PLEATHER

### 5.3.2 Chromium removal from leather

Chromium extraction from leather was studied. We used mainly carboxylic acids as extractors, and the best results obtained so far were for citric, tartaric and oxalic acids. The pH and the temperature of extraction have to be chosen as a compromise to maximize the extraction without significant gellification. For citric acid at a pH of 4 and at a temperature of 60°C with a 20-fold excess of citric acid, extractions as high as 90% were obtained after two consecutive operations. Nevertheless, these studies are not yet complete, as the amount of chromium removal is highly dependent on the tanning conditions and on the size of the scrap particles. Further work is expected in this area to gain insights into physical pre-treatments of scrap leather that lead to maximum chromium removal and also on the development of a continuous extraction system.

## 5.4 CONCLUSIONS OF SCIENTIFIC RESEARCH ON PLEATHER

1 It is possible to produce thermoplastic leather--PLEATHER--from ground hides and leather scrap by destroying a part of the collagen fiber structure. PLEATHER is a reasonably strong and hard material compared to nylon 6/6. A simple model pertaining to fibrils (0.1 μm) is useful for explaining certain microstructures and some of the behavior of PLEATHER.

2. It is advisable, although not absolutely necessary, to dechromize the chrome tanned leather scrap before making PLEATHER.

3. Certain production parameters--temperature, pressure, and time--are dependent on the raw material and the state of the fiber material.

4. The influence of temperature on production is much stronger than the influence of the other parameters.

5. PLEATHER is resistant to common chemicals, but is extremely sensitive to water. The influence of water has been demonstrated but needs further careful investigation, both during production and subsequent use.

6. A separate research on mass-production techniques of PLEATHER has to be performed.

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# 6 IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

by Baltazar de Castro, Portugal.

The answer to this point will be addressed in two main areas, one concerning the impact in my laboratory and the second reflecting possible industrial applications.

The participation of my laboratory in this project represented a starting point in a new research direction – that of applied chemistry/chemistry of materials. Through the development of the project, fundamental new techniques were used by us in Porto to characterize the new materials produced. Although, electron microscopy ( either SEM or TEM ) was a well established technique here, its application to the study of polymeric materials has not been extensively used; from our point of view it opened up the possibility to study other natural occurring polymers ( cellulose and polysaccharides ) and thus to complement our chemical studies on these substances. We tried, also, to apply to the characterization of polymeric material the methodologies used for the study of biomolecules, namely we implemented gel electrophoresis, gel permeation chromatography and HPLC. These techniques, specially HPLC/size exclusion chromatography, show also great potential to study other polymeric materials. We can claim to have acquired/developed the methodologies to tackle the problem of organic polymer characterization in solution and in the solid state, and we hope to be able pursue this line of work with novel materials.

On what concerns the second point, it is necessary to point out that the annual production of tanned leather scrap in portuguese tanneries is about ten thousand metric tons per year and that about eight thousand tons of scrap leather is also produced by the shoe industry, and that this amount of solid waste poses great environmental problems, mainly in two specific regions : Porto metropolitan area and Alcanena. So, the possibilities to transform this solid waste in a high-valued material may have, besides the technological benefits of developing a material with novel properties, a tremendous impact in cleaning up the environment. There are two draw backs to the implementation of *pleather* production at industrial scale : first, the removal of chromium, a key factor if *pleather* is to be made from chrome tanned leather, was not completely solved, although final chromium concentrations as low as 0.05 % were obtained in laboratory tests; and second, no pilot plant studies were conducted to optimize the operational conditions and to address the simultaneous use of leather scrap from different sources.

PROJECT ACTIVITIES/OUTPUTS

Three scientific meetings were held at Porto University and two at the Jerusalem College of Technology. Dates:

January 1988 - Jerusalem

September 1988 - Porto

January 1989 - Jerusalem

May-June 1989 - Porto

April 1990 - Porto

At no expense to the CDR budget we visited the Semaine de Cuire in Paris (September 1988) where we made contacts with leather producers from developing countries (Kenya, Thailand, India, Zimbabwe).

Furthermore, one of our engineers visited the Technical University of Darmstadt, Germany, for discussions with Prof. Heidemann, who is a leading collagen specialist, and the TNO Leather Institute in the Netherlands, where the use of leather scrap and the dechromization of chrome tanned leather were discussed.

A report on possible applications of the developed technique in environment clean-up was presented by Baltazar de Castro in an invited lecture at "V Encontro Galego-Portugues de Quimica" held at La Coruna (Spain) 21-23 November 1991, and entitled "Aproveitamento de residuos solidos da industria dos curtumes por transformacao num material termoplastico" (Recycling of leather scrap from tanneries by transformation into a thermoplastic material).

Frequent contacts between the principal investigators were made by FAX and telephone.

In discussions with several large leather firms it was ascertained that the profit margins in the leather industry are too low to permit investments in R & D.

Publications: To date four papers have been published, two more have been accepted for publication, and two have been submitted for review. Publications number 1-6 are appended to this report along with a draft of publication number 7.


1. R.T. Markus, A. Duman and A. Wyler, The influence of additives on hot pressed leather-PLEATHER, J. Soc. Leather Technol. Chem., 74, 74 (1990).
2. A. Wyler, R.T. Markus and B. de Castro, A model for the internal structure of hot pressed leather, J. Soc. Leather Technol. Chem., 75, 52 (1991).
3. A. Wyler, R.T. Markus and B. de Castro, Variations in the microstructure of hot pressed ground leather--PLEATHER, J. Soc. Leather Technol. Chem., 75, 126 (1991).
4. A. Wyler, R.T. Markus and B. de Castro, Microscopical observations on thermoplastic leather--PLEATHER, Shoe Techniques, 85, 879 (1991).
5. A. Wyler, R.T. Markus, H.J. Wagner, B. de Castro, Matrix Autoreinforced Organic Material--MARIOM, J. of Mat. Res., In Press.
6. A. Wyler and B. de Castro, Microscopical Views on the fusion bonding of vegetable tanned leather parts, J. of American Leather Chemists Assoc. JALCA, to be published.
7. B. de Castro, M.A. Ferreira, R.T. Markus and A. Wyler, Influence of processing temperature and pressure on stability of the structure of hot pressed ground leather, submitted for publication in J. Appl. Polym. Sci.
8. B. de Castro, M.A. Ferreira and A. Wyler, Molecular weight distribution in hot pressed ground leather determined by size eclusion chromatography, to be submitted for publication in Polym. Eng. Sci.

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## 8. PROJECT PRODUCTIVITY

We consider the proposed goals of the project: 1) Characterization of a novel thermoplastic material made of hides and leather scrap; 2) The formation of a scientific group for the research of leather at Porto University, which was the wish of the Portuguese Tanners and Leather Association; and 3) Arousing interest in developing countries for using their indigenous leather scrap for making a useful material, as having been accomplished.

## 9. FUTURE WORK

The project will lead to future work in:

1) Research on a new concept for making in situ composite materials, made of natural fibers. (AID-CDR. Cg-199)

2) Research on the removal of chromium from chrome-tanned leather and reusing the precipitated chromium for chrome tanning of hides to form a closed system.

3) Hopefully (and strongly advised) research on the development of production techniques for producing thermoplastic leather, PLEATHER, from scrap.

## 10. REFERENCES


1. R. Leberfinger, Doctorate Thesis, Darmstadt, Germany (1964).


xg31/aid.wyl

*Journal of the Society of Leather Technologists and Chemists, Vol. 74, p. 74.*

# THE INFLUENCE OF ADDITIVES ON HOT PRESSED LEATHER–'PLEATHER'

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**Summary**

A novel process has been developed to produce 'hot pressed leather fibre composite', a new material, from leather scrap.

Characteristic of the process are the raw material, scrap of mixed tannages skin or hide, reduced to fibers, and the process parameters, namely temperature and high pressure. By use of additives and by changing the process parameters, the internal structure and mechanical properties of this new material may be changed.

Ageing of the material, apparent in the change of its mechanical properties and its structural background has been investigated. Ageing studies revealed the compatability of additives with the raw material. Because of the relationship of the material to both plastic and leather, the term *Pleather* was coined to designate the material

## Introduction

A process has been developed, the basis of which is that at elevated pressures and temperatures dry leather fibre is converted to a material that behaves rheologically like a thermoplastic. That is, it will flow under heat and pressure instead of decompose. Judiciously selected additives and process parameters, temperature and pressure, determine the properties of the material, the rheological behavior in the production stage and the properties of the final product. Most of the additives investigated, selected on chemical grounds, are well known in the leather and the plastics industries.

The phenomenon of ageing was also studied. Ageing took place in air, water and machine oil, all at ambient temperature. The most probable ageing mechanism of the material has been described.

The new material could be utilized as a replacement for leather, plastics and rubber. Other possible applications of Pleather may take advantage of the fact that it is based on a bio-material and, therefore, it is a potential material for implants when bio-compatability is a prime requirement.

Pleather may be produced, using plastic forming techniques.

The major advantages of *Pleather* are that:

1 The material can be made into intricate shapes through conventional production techniques, such as compression, and injection molding.
2 The grade of Pleather, specified by physical and mechanical properties, can be determined by prescribing process parameters and additives.
3 The possibly ecologically harmful, raw material is cheap and readily available. It could be scrap of either tanned or untanned skin or hide.

A preliminary costs analysis showed that producing articles of Pleather, would be cost competitive with producing them of leather or common plastics.

## Experimental Methods and Their Rational

*Pleather* has been produced from cowhide, goat and sheep skin both untanned and vegetable tanned, mixed (both vegetable and chrome) tanned and with glutaraldehyde.

1 *Raw Materials:* Mixed-tanned leather (both vegetable and chrome tanned), comminuted in a Wiley mill, constitutes the raw material with which chemical additives are mixed. The ground material contains only fibrous material of approximately 5 mm length, with no lumps – larger particles absorb the bulk of the additives thus impeding their effective distribution throughout the raw material.

2 *Chemical Additives:* For the purpose of equal distribution of the additives throughout the ground material, ethyl alcohol was added. Ethyl alcohol is a good penetrant due to its short chain length, and a good surfactant, enhancing the wettability of the fibres. Furthermore, all additives, used up to now, can be completely dissolved in ethyl alcohol which will also contribute to their penetration and absorption. Alcohol appears to act as a temporary plasticizer* too, fluidizing the material in its production stage. At concentrations of over 12% the viscosity becomes so low, that it fills gaps between parts of the mould of less than 0.01 mm.

Molded Pleather becomes stiffer with time due to evaporation of the plasticizers, like ethyl alcohol. Butyl, hexyl and octyl alcohol proved ineffective as they are hydrophobic, whereas the raw material is hydrophilic. Methyl alcohol, which is toxic, was not used. Glycerol, also an essential component, is used for its lubricating properties enabling fibers to slide along each other making the material more flexible and resilient. The minimum effective concentration of glycerol is approximately 4% by weight. At high concentrations glycerol exudes from the material during processing. At concentrations over 15% the problem of ageing – deterioration of properties, like flexibility and resilience, and the onset of brittleness – seems to be halted, provided that the processing temperature has been kept at the correct level.

* A. Duman z.l. deceased.

* The term plasticizer is used in accordance with the description given in the Modern Plastics Encyclopedia where the softening action of plasticizers 'is attributed to their ability to reduce intermolecular attractive forces of the polymeric system'. Two mechanisms are mentioned, the first nullifying intermolecular bonds, the second forcing the polymer molecules apart.



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Long chain chemicals with large numbers of OH groups attached to their chains were expected to be reactive with collagen molecules. For this reason the influence of polyethylene glycol (1000) and polypropylene glycol (2000) was tested, neither additive proved useful. The addition of ethyl alcohol, in which both dissolve, proved ineffective.

Sulphur is known to react with collagenous material. Therefore, thioglycolic acid, was selected, which has a sulphur atom and a OH – group attached to its chain. This chemical proved to have a very powerful influence on the flexibility of the samples, with concentrations of over 1.5% (by weight) yielding material of a flimsy structure. The acid is thought to break the hydrogen bonds between the polypeptide links.

Demineralized water proved effective between 10 and 15% based on the dry weight of leather fibre, at concentrations below 10% no change of properties was observed. At increasing concentrations flexibility improved, much as is the case with ethyl alcohol. At high concentrations, inherently weak gelatin was formed.

3 *Preparation of Raw Material*

Before processing, the raw material is mixed with the additives. Mechanical mixing was achieved by means of a slowly rotating magnetic stirrer. During the stirring operation, the material was kept in a beaker, sealed off with plastic foil in order to prevent moisture absorption from the air by the hydrophilic additives. Observation of a certain interval between mixing and processing allows the additives to diffuse throughout the material and penetrate into the fibres. The optimal dwell time is 48 h after which dispersion of the additives is uniform. An attempt to speed up the diffusion process was made by heating the leather fibres, mixed with the additives, for 5 hours at 50°C. The result was that the additives were completely absorbed and concentrated in isolated areas. Outside of these areas, Pleather with different properties was formed, uninfluenced by the additives.

## Production Process of Pleather

After the dwell time the mixture is compressed at a pressure exceeding the process pressure in order to compact the material. Compaction facilitates penetration of the additives during processing. After settling the pressure is lowered to the process pressure, a few hundred bar, and the press is heated up. The process temperature is over 70°C.

Before and during the production phase, compression and heating take place in a mould that can be either heated electrically, or cooled by water. Pressure is measured with a load cell. The temperature is measured by a thermocouple.

In order to check weight loss, the prepared material is weighed before and after processing. During the process the following variables are recorded:

1) initial temperature, 2) maximum temperature reached, 3) the time at which this occurs, 4) the maximum pressure, 5) the time that elapses, before the temperature reaches its process value (at which it is kept constant), 6) the pressure, 7) the temperature at the onset of cooling, 8) the time during which the process temperature is maintained.

In most cases the process takes 8 min, beyond this period the final material structure does not display any further changes.

The second and third variables are taken in order to detect deviations from the set parameters and their possible influences on the structure and material properties. The sixth variable is taken as an indicator of phase change in the material during processing – the pressures change, dependent on the additives and the heating time. Very low viscosity melts show a sharp pressure drop due to the phase change. The remaining measurements are used to document the course of the production process. After the preset time, the sample is cooled and inspected.

The following data give a practical example of process parameters:

| | |
|---|---|
| 1 Initial Temperature: | 21°C |
| 2 Maximum Temperature: | 101°C |
| 3 Time at Process Temperature: | 3 min. |
| 4 Time at Maximum Temperature: | 3.5 min. |
| 5 Pressure: | 245 atm. |
| 6 Temperature at Cooling: | 101°C |
| 7 Process Time: | 8 min. |

The water vapor permeability according to IULTC Official Method IUP -15 is about 0.7 mg/cm$^2$/h, which is more than one order of magnitude lower than with leather. This sample has been remolded at 120°C and 300 atm. for 6 minutes.

## Assessments of Properties

1 *Structural Properties*

It is mandatory that the material be homogenous throughout, both with regard to the distribution of the additives, and with regard to the absence of agglomerates or other discontinuities. The homogenous nature assures isotropic mechanical properties.

With certain chemical additives not only their concentrations, but also their ratios proved important. This is so with ethylene glycol and propylene glycol. At a ratio of 2:1 they enhance the homogeneity of the material's structure as well as the dispersion of the additives throughout the material, moreover, as the concentration of both increases, the material becomes more flexible.

The influence of the molar ratio of the additives, glycerol and thioglycolic acid becomes apparent in the toughness of Pleather when 1 part of thioglycolic acid to approximately 3 parts of glycerol are added. It was found that, when glycerol and thioglycollic acid are mixed and added to the raw material after several days, the toughness is increased significantly, possibly due to ester formation.

A quite separate phenomenon was the formation of voids on the surfaces of samples. The craters are produced by trapped vapours – mostly water and ethyl alcohol, as the boiling point of the other additives lies well above the processing temperatures. In order to produce a smoother surface, the pressure on the material is completely relieved for a few seconds after the process temperature is reached. This allows the trapped vapors to escape from the mould. Voids within the material are very rare.

2 *The influence of ageing on mechanical properties*

**2.1 Definition of mechanical properties**

In order to determine possible applications, we investigated several mechanical properties as listed below:

*Quantitatively determined properties*

Indentation hardness (Shore D): the initial hardness is measured at ambient temperature, a drop in this value during measurement is a measure of cold flow or creep.



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*The qualitatively investigated properties are:*
Resilience: the capability of material to absorb energy through elastic deformation as measured by its ability to recover its original shape after being deformed.

Flexibility: the test comprised measuring the angle over which the material could be bent without plastic deformation or cracking.

### 2.2 Ageing

The change in certain of the above properties was recorded as a function of time in an environment of air, water or oil, also recorded was the change in the weight of samples.

Regarding the increase with time of brittleness, the influence of the dwell time is very pronounced. A dwell time of 5 min results in samples with a much higher hardness (Shore D-scale), than does a dwell time of 48 h. This difference remains throughout the ageing process. The reason being that during the 48 h the ethyl alcohol and other additives penetrate much more deeply into the fibres, and so their influence on the final material properties is more marked. Thus, a sample that was made with a dwell time of 5 min aged more quickly than the other samples. Its final hardness approaches the hardness of a sample of Pleather that produced from leather using the same process parameters, but without additives.

The fibre length of the raw material influences the hardness and the ageing parameters. As the fibre length increases, so does the material hardness, while the ageing process is attentuated. Typically, the hardness of samples made with 5 mm. long fibres is 4 points higher on the Shore D scale, than the hardness of samples made with 1 mm. long fibres.

When air ageing, weight loss may signify evaporation of additives, whereas weight increase may indicate oxidation of additives, or absorption of water vapour from the air either by Pleather or its additives. Ageing at constant weight may be due to a slowly proceeding chemical reaction, or due to above mentioned phenomena, taking place concurrently and cancelling out each other's influence on the weight change. Thus, results based on weight changes are not conclusive.

The flexibility of the material improves as the ethyl alcohol concentration is increased without changing the concentration of the other additives. However, higher concentrations of ethyl alcohol incur progressively larger weight losses within 24 hours of processing. After 96 hours all samples showed successive weight increase.

As the additives penetrate into the leather fibres during the dwell time, the ethyl alcohol mixes with, amongst other things the water which is naturally present – between 12 and 20% of the weight of dry leather at R.H.30–70%.[2] After processing, water and ethyl alcohol evaporate simultaneously, as a mixture for a period of between 36 and 72 h, thus the water concentration within the Pleather sample is reduced to below its equilibrium value. This fall in moisture content is completely restored within 96 hours after processing, as water vapor is absorbed from the air. Table I shows both the initial weight loss, due to evaporation, and the successive weight increase, due to vapour absorption from the air.

Water ageing: samples were soaked in water at 18°C for 24 h and left to air dry at 18°C for 48 h, comparison of the weight of samples before soaking and after drying

TABLE I
**Changes in weight of pleather samples with time**

| Alcohol concentration in mixture (%) | Initial weight loss (%) | Successive weight increase after 96 hours (%) |
|---|---|---|
| 6.8 | 8.7 | 3.3 |
| 12.8 | 10.7 | 9.6 |

reveals that the weight loss is 25 to 30%. Certain components added either, during the tanning process, or added as additives – probably the water soluble glycerol and ethyl alcohol – are dissolved and extracted from the samples, as the glycerol and ethyl alcohol content in all samples was the same, all were affected similarly by their stay in water. Due to the chemical change of the Pleather structure, all of the water aged samples became very hard after drying, like leather,[1,2] in the course of a few weeks.

Table II lists the hardness of the samples, immediately after removal from water, and after three months as a function of the ethyl alcohol concentration.

Samples to which thioglycolic acid was added, a powerful plasticizer as mentioned above, display a similar pattern, the plasticizing influence shows up well in the lower Shore D values, see Table III.

Soaking samples in oil (initially containing 22% ethyl alcohol), produces results similar to those found with air ageing. After 82 days in machine oil the hardness was only slightly lower than the hardness of the same samples that aged in air for 92 days. In Table IV too, the influence of thioglycolic acid is dominant.

## Discussion and Conclusions:

The principal effects of the process parameters and the additives, investigated in the present work, may be summarized as follows:

1 It is possible to change the structure of the composite investigated by heating it while applying pressure whereby polymerization takes place, incurring changes in structural and mechanical properties:

2 Through the addition of specified chemicals the properties of the newly produced material may be changed although, it must be emphasised that chemical additives are not a pre-requisite.

3 The length of the leather fibres also influences the mechanical properties of the fully processed material. Longer fibers provide interlocking and cross-linking in more locations for each fiber. This becomes apparent immediately after processing as samples are more flexible when shorter fibres are used. However, the more complex structure that is reached with longer fibres resists ageing better.

TABLE II
**Change in hardness with time**

| Ethyl alcohol concentration [%] | Hardness, t = 0 h [shore D] | Hardness, t = 3 months [shore D] |
|---|---|---|
| 6.8 | 70 | 73 |
| 12.8 | 72 | 73 |
| 22.7 | 78 | 76 |

TABLE III
Changes in hardness with time

| Ethyl alcohol concentration [%] | Thioglycolic acid concentration [%] | Hardness t = 0 h [shore D] | Hardness t = 3 months [shore D] |
|---|---|---|---|
| 6.6 | 3.3 | 50 | 77 |
| 12.4 | 3.1 | 53 | 76 |
| 22.1 | 2.8 | 37 | 67 |

TABLE IV
Changes in hardness with time in air and oil

| Ethyl alcohol concentration [%] | Thioglycolic acid concentration [%] | Hardness | |
|---|---|---|---|
| | | 92 days in air | 82 days in oil |
| 22.7 | 0 | 76 | 72 |
| 22.1 | 2.8 | 67 | 53 |

4 While water can be used as a temporary plasticizer in the production of Pleather, gelatin is formed at high concentrations. The gelatin coats the fibres, that make up the material. This weakens the inherent bonding forces between them.

5 Rigid Pleather does not undergo any perceptible ageing with respect to change in mechanical or physical properties. Flexible grades, however, do age. In order to alleviate this effect which is probably due to the evaporation of additives, higher boiling plasticizers will be introduced.

6 Dependent on the process parameters, polymerization may be allowed to affect all the leather fibres, to be processed, or only a part of them. With partial polymerisation unchanged fibres act as to reinforce the Pleather matrix, much as glass, carbon, or aramid fibres serve in composite materials. Here an elegant method has been found for the 'autoreinforcement' of the matrix, reinforcement by means of compatible fibres made from the same basic material as the matrix itself.

The resulting mechanical properties of 'autoreinforced' Pleather depend on the fiber length and the degree of fiber polymerization. The desired degree of polymerization may be obtained by judiciously choosing the process parameters.

## Acknowledgement

We wish to express our gratitute to Mr Y. Frankl, Head of the Leather Department of the Israel Fibres Institute for useful discussions.

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# A MODEL FOR THE INTERNAL STRUCTURE OF HOT PRESSED LEATHER

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**Summary**

By subjecting scrap of mixed tannage skin or hide, previously reduced to fibres, to pressure and heat the internal structure of this raw material changes markedly going through well definable, consecutive phases.

In this article the specified phases are described. By means of a simplifying model several unexpected phenomena that were observed with a Scanning Electron Microscope (SEM) are explained.

## Introduction

In a previous article in this journal,[1] we reported on the development of a new material, 'Pleather', hot pressed leather fibre composite, based on leather scrap. The present article discusses the internal structure of this material, produced from mixed tanned bovine hide.

Properties of materials are determined by their internal structure. Therefore, in order to develop optimal values of mechanical and physical properties in a rational way, an understanding of the influence of process parameters on the internal structure is necessary. With hot pressed fibre composite this structure showed up as partially fibrous and partially continuous. A model is used to explain the mechanism of how some of the observed structures evolve from the raw material.

## The internal structure of Pleather

### 1) *A Model of the Internal Structure*

Leather, as is well known, is built up of fibres. The SEM micrograph in Fig. 1 shows the internal structure of mixed tanned bovine hide, the raw material we use in our experiments. For clarity we subdivide the structure of leather fibres that have a diameter ranging between 5 and 10 $\mu$m, into two categories[2], see Fig. 1:

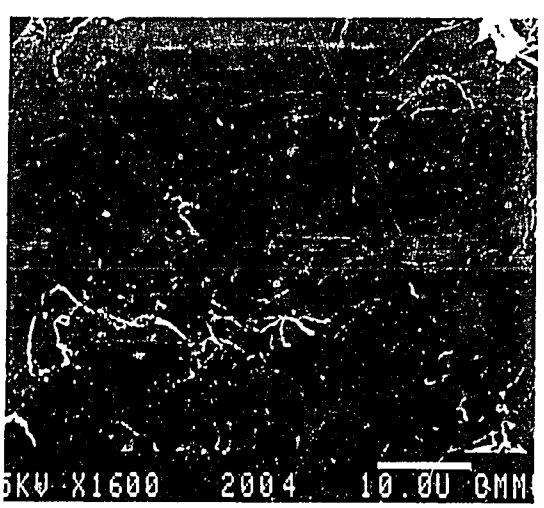


**Figure 1.** Micrograph of unprocessed, mixed tanned bovine hide: fibres (diameter: 5–10 $\mu$m), primitive fibres (diameter: 0.1–0.5 $\mu$m) and fibrils (diameter: 0.1 $\mu$m).

1) primitive fibres with a diameter between 0.5 and 1.0 $\mu$m, arranged in parallel helices.
2) fibrils with a diameter of about 0.1 $\mu$m, that make up the primitive fibres.

Here we will use a model of a leather fibre, made from kneadable 'Plasticine', in order to demonstrate what happens within the internal structure when an outside pressure is applied. In Figs. 2a and 2b the round Plasticine cylinders represent the primitive fibres of a leather fibre. Comparison between the Plasticine model and the actual leather structure of a leather fibre shows the following (dis)similarities:

| *Similarities* | *Dissimilarities* |
|---|---|
| Round cross sectional shape of primitive fibres and plasticine cylinders | |
| The external shape of both can be changed under influence of pressure | Plasticine is shapeable at room temperature, leather fibres at elevated temperatures. |
| In bovine leather the primitive fibres run parallel to each other and so do the Plasticine cylinders | In bovine leather fibres the primitive fibres are twisted, in the model the cylinders are straight. |

It is impossible to completely fill space with round cylinders as there will always remain free spaces between them. An external pressure from above can be exerted on the Plasticine cylinders, as shown by the arrows, the effect of which is parallel to what happens to leather fibres in our laboratory press. Before compaction, contact between neighbouring Plasticine cylinders is along narrow, longitudinal planes, that broaden under pressure, as seen in Fig. 2c. Here the interstitial spaces are partially filled. At first horizontal planes evolve, perpendicular to the direction of the exerted forces. As the cylinders expand under compression, they also exert lateral forces on each other, and so vertical contact planes too were formed, see Fig. 2d. Thus, originally round primitive fibres assume rectangular shapes. As



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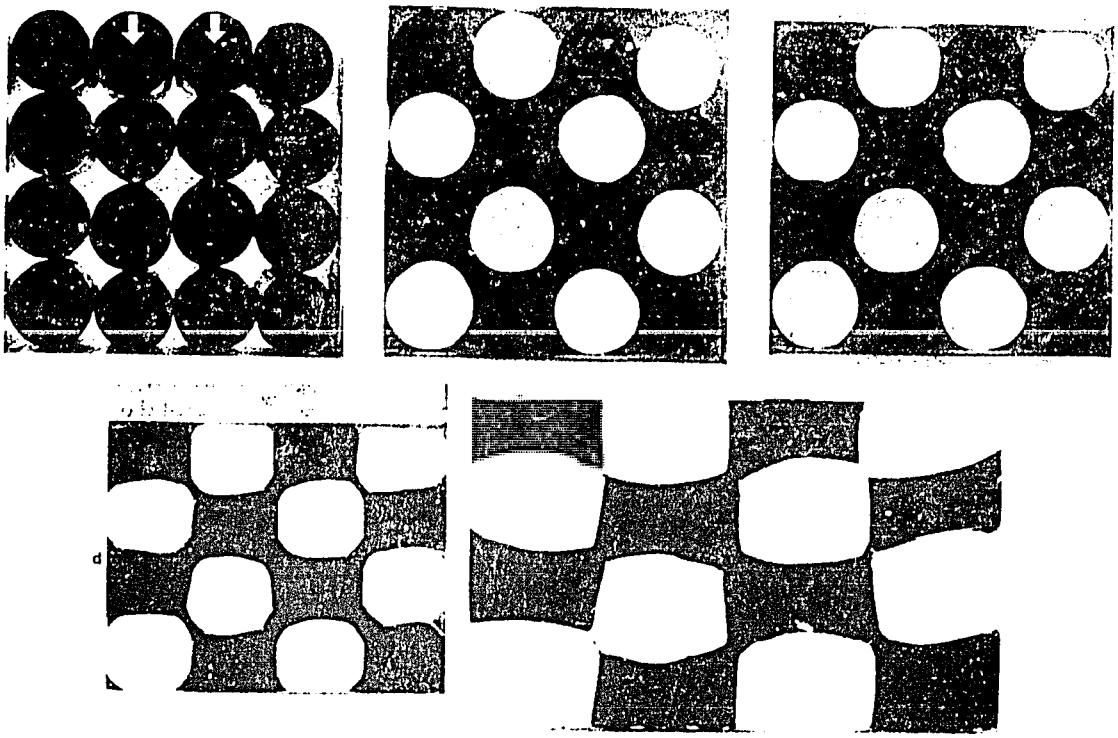

**Figure 2.** Simulation of the evolution of rectangularly shaped formations under influence of pressure and temperature.
Figure 2a and b The originally round plasticine cylinders, representing parallel primitive fibres. Figure 2c horizontal contact planes are formed, due to pressure exerted from above. Figure 2d The following stage where where vertical contact planes exist too. In Figure 2e The final stage is reached, where the interstitial spaces have been all but completely filled.

stated before, round shapes cannot completely fill a space, however, as seen in Fig. 2e, rectangular shapes do!

Returning to leather fibres, we may expect that, due to the application of heat and external pressure, round primitive fibres will be transformed into rectangular ones, that may fuse together to form a continuous material. If the pressure is not sufficiently high, the material will remain fibrous.

2) *Observation by SEM*

With a scanning electron microscope (JEOL JSM-35C) the internal structure of Pleather was studied. The Pleather samples were coated by sputtering with gold. The resulting layer was 200 Å thick.

The SEM micrograph in Fig. 3 shows a sample that has been processed at 50 atm. and 110°C. Several phases in the transformation from fibrous material to continuous material can be observed. The different morphology of each phase depends, i.a., on the process pressure. At the right the fibrous structure has retained its original form. Fibres, primitive fibres and fibrils can be clearly seen. Location (5 6, A B)* shows the transition from the fibrous material to the continuous material. In (1 4, A) continuous material was formed. Here the material's morphology is quite irregular and appears to be composed of stacked, flat particles, and around 2,E particles with right angles may be observed. At 1,E,G the material is formed into particles with right angles, resembling

**Figure 3.** Successive phases in the transformation from leather to the continuous material. Pleather: fibres, split into primitive fibres, flaky material, cubes and continuous material. Clearly noticeable is a cube at (5, L).
Process pressure 50 atm. Temperature 110 C, magnification = × 3600. The length of the bar represents one hundredth of a millimetre (= 10 μm)

squared beams and cubes. At the bottom of the picture, the structure of this sample reached its furthest developed stage. Here the structure is continuous and is built up of fused, rectangular particles. Most noticeable is the cube at 5,L.

The micrograph in Fig. 4 shows the continuous phase, produced at 600 atm. and 150 C, which makes up the

* Locations are indicated by means of coordinates next to each micrograph. 5 6 or A B indicate the intermediate space.



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**Figure 4.** Continuous material, Pleather with holes and straight edged formations.
At (1, F) two primitive fibres crossing one another. Process pressure 600 atm, Temperature 150°C, magnification = × 5400. The length of the bar represents one thousandth of a millimetre (= 1 μm).

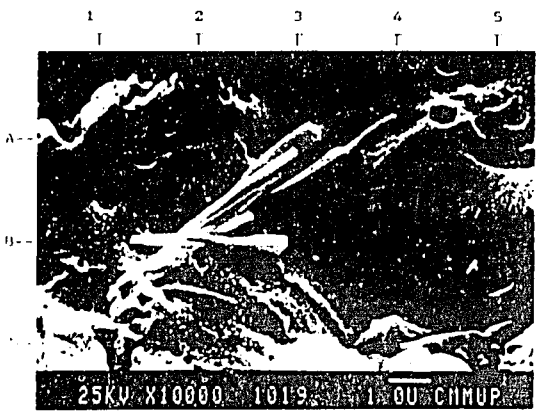


**Figure 5.** Primitive fibres crossing one another.
Several primitive fibres show a rectangular cross section. The background consists of continuous material, Pleather. Pressure 650 atm, Temperature = 120°C, magnification = × 10 000. The length of the bar represents one thousandth of a millimeter (= 1 μm).

bulk of the material. Here too, particles with right angles are dispersed throughout the material. At 2,A the protruding tip of a beam is observed. The formation of the continuous phase is here also the final stage in the formation of Pleather from the fibrous material under the prevailing conditions. This is the stage where rectangular particles become an integral part of the continuous phase as in locations 3,A and 4,D. At 5,F G this transition process is seen to have taken place within a conglomerate of fibrils that together originally formed a primitive fibre. This transition process also took place between the conglomerate and the already existing continuous material, as can be seen at 3,A. At 1,F and 3,A the process is also seen to have taken place between separate, intersecting fibrils.

At a magnification of × 10 000, as in the micrograph of Fig. 5, it may be observed that also fibrils obtain a rectangular cross section and form continuous material. 2,B, here at 650 atm. and 120 C. Intersecting fibrils are also shown in this figure.

The 5 μm holes as well as the smaller ones in the continuous material are probably caused by gases, produced during the process.

## Discussion

### 1) *General*

Consecutive phases in the formation of Pleather are shown in Fig. 3. Where, due to the large interstitial spaces, the local pressure remained below the applied average pressure, the fibrous structure is still visible. When local pressure is higher, continuous material was formed, already displaying regular shapes. Still higher local pressures cause cubes to be formed.

### 2) *Formation of cubes*

Cubes and other geometrically shaped particles, with about 1 μm long edges (see micrographs in Figs. 3,4,5,6) are puzzling. Those shapes are almost exclusively found in Pleather made from mixed tanned, bovine leather. Extensive investigation of material made from glutaraldehyde tanned sheepskin showed this phenomenon on only one occasion.

The following hypothesis on the formation of cubes in bovine fibre based material is put forward. Under the influence of pressure and heat the fibres of about 5 μm diameter, see Fig. 1, are first split into primitive fibres, which are then shaped into beams with a rectangular cross section, and edges of about 1 μm, as explained in the section on the Model.

Fibre bundles in bovine hide are not parallel, but run through the structure under different angles, called weave angles. In Fig. 7 a sketch of possible structures of fibres with respect to their weave angle is given. A high weave angle of between 70° and 80° is characteristic for thick bovine hide, a low weave angle close to 0° is characteristic for sheepskin.[3,4] Fibres cross at 'knots', see Figs. 4 and 5. These knots are locations of relatively high stress concentrations. When an external pressure is applied on Pleather, where weave angles are sufficiently high, the now rectangular primitive fibres shear off at the knots, and cubes are formed. In Pleather made from sheepskin fibres the formation of cubes rarely occurs due to the low weave angle.

Triangular shapes, Figs 4 at 3,A and flat shapes,

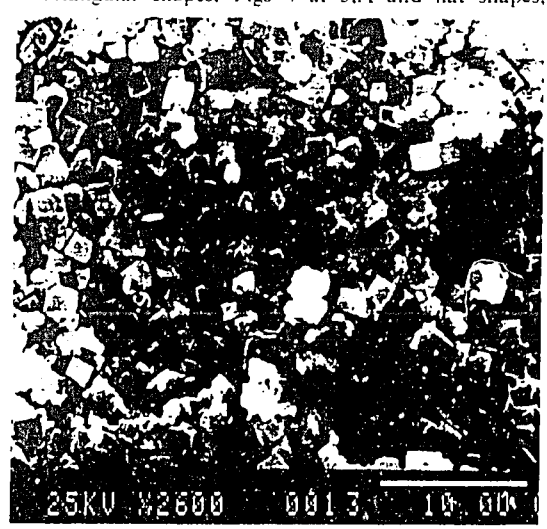


**Figure 6.** Agglomeration of geometrically shaped particles, many of which are blocks with right angles.
Pressure 50 atm, Temperature = 110 C, magnification = × 2600. The length of the bar represents one hundredth of a millimeter (= 10 μm)

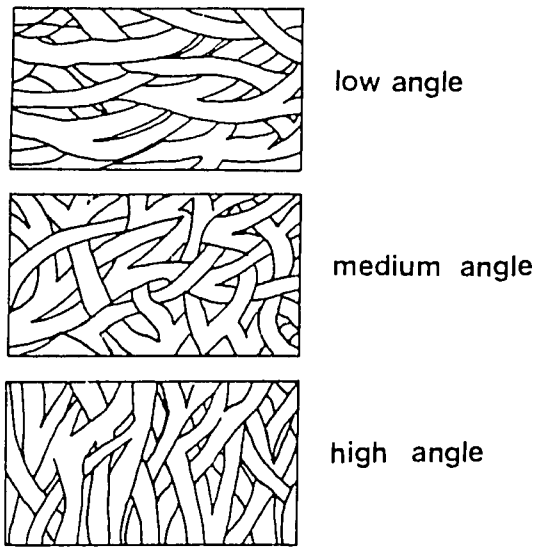


**Figure 7.** Three categories of dermal weave angle at which fibre bundles interweave. High weave angles are characteristic of bovine hide. Sheepskin typically shows low weave angles.[3]

Fig. 3 at 1,4,A were also found. These are formed due to non-isostatic pressure within the material. Due to its symmetrical construction and the uniform pressure the model shows mostly rectangular cross sections.

## Conclusions

1) By using round Plasticine cylinders a simple model was constructed, an analogue of the structure of a leather fibre.

2) With this model the influence of external pressure on leather fibres could be simulated. It was shown how round fibres become rectangular.

3) The formation of rectangular shapes, as observed with the SEM, can be explained with the Plasticine model. Leather fibres are transformed to either rectangular beams or triangular or flat shapes with which the space can be completely filled. This results in the formation of continuous Pleather matrix material in which unconverted leather fibres are present.

## Acknowledgements

The help of Mr. Carlos Sá from the Department of Electron Microscopy at the University of Porto with the SEM work is gratefully acknowledged.

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# VARIATIONS IN THE MICROSTRUCTURE OF HOT PRESSED GROUND LEATHER, 'PLEATHER'.

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**Summary**

The morphology of hot pressed, ground leather fibre depends on the process parameters, pressure and temperature, and is also influenced by the stress distribution within the material during processing. In this article several factors, influencing this distribution are discussed. Further load *vs.* compression curves are also presented.

## Introduction

In previous articles we have discussed the influence of additives on a hot pressed leather fibre composite material, Pleather[1] and presented a model for the internal structure thereof.[2] Here we discuss Pleather that has been compressed at temperatures of around 100°C.

We shall expand on the structure of this material which may display itself in different ways, as seen in the scanning electron micrographs. Our objective is to study the material structure as a function of processing parameters only. Therefore, additives like plasticisers, as discussed previously,[1] were not used. For the same reason the leather particles were not moistened, or dried prior to processing. The equilibrium moisture content is approximately 12%. We shall also discuss the underlying principles that influence the morphology of hot pressed, ground leather. It will be shown that the manner in which stress is distributed throughout this material, has a predominant influence on the appearance of the final structure. Further, we shall present load-compression curves of Pleather and leather for reciprocal comparison.

## Factors causing variations in the microstructure of hot pressed, ground leather fibre

The different formations of the microstructure of hot pressed, ground leather are the results of two main phenomena:

1) Leather is built of various 'building blocks' that are disentangled under influence of pressure and heat,
2) Non-uniform stress distribution throughout the material during processing.

For the production of hot pressed, ground leather, leather is comminuted in a preparatory stage, whereby its fibres are cut. Cut-off ends are shown in Fig. 1* at (B/C,3/4), (G/H,4/6) and in Fig. 2 at (F,1), (F/H,4/5), and at (G,3). These ends facilitate the unravelling of the fibres in the processing stage, where its components are separated under influence of mechanical and thermal energy. This applies especially to the fibrils, which depending on the direction of the internal stress, may either be tightly 'pushed' around the surface of their primitive fibres, or unwound and loosened. In the processing stage these compressed particles either retain their fibrous character, when the local pressure is insufficient (Fig. 2 at the left), or, at sufficiently high pressures, are transformed into a viscous substance.

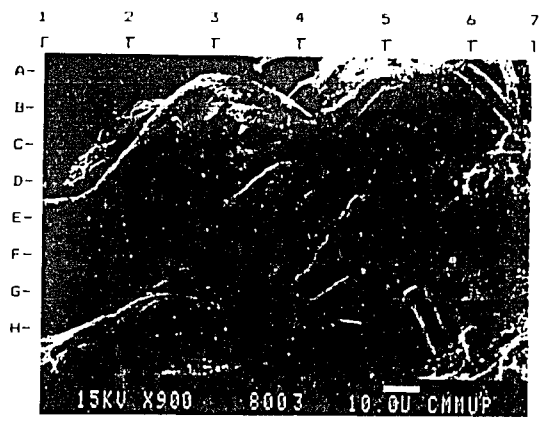


Figure 1. Ground mixed tanned bovine hide showing cut-off fibre ends. Magnification: ×900. The length of the white bar represents one hundredth of a millimetre (= 10 μm).

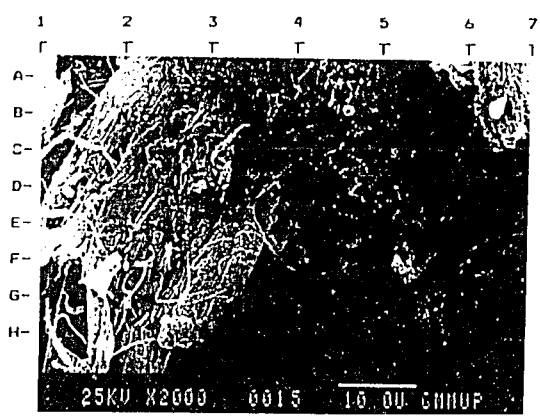


Figure 2. At left unchanged fibres. At right a structure solidified from viscous primitive fibres and fibrils. External process pressure: 50 atm, Temperature: 110°C, time: 6 minutes, Magnification: ×2000, Bar equals one hundredth of a millimetre (= 10 μm).

Note: Leather is constituted from fibre bundles, which consist of twisted fibres (diameter between 5 μm and 10 μm), that themselves are composed of twisted primitive fibres (diameter between 0.5 μm and 1.0 μm) (see Fig. 1.). On an even smaller scale fibrils (diameter of less than 0.1 μm) make up the primitive fibres.

* Locations are indicated by means of coordinates next to the micrograph. 1/2 or A/D indicate intermediate spaces.

which becomes increasingly fluid as the process temperature increases. On cooling such an intricately structured viscous matter consolidates the final structure of Pleather, a sample of which is shown in Fig. 2 at the right. The process parameters for the specimen of Fig. 2 are P = 50atm, T = 110°C, t = 6 min.

Non-uniform stress distribution may be caused by:

a) voids within the compressed material. The voids originate from:

—the non-compact structure of leather.
—the random directions of the particles, preventing 'close-packing' under compression.
—fibres, that were pulled out of the material. These voids prevent the external pressure from reaching all the material in the die.

b) during processing the compressed particles comprise neither a rigid material, nor a liquid, but are in an intermediate, viscous state:

When an homogeneous, rigid material is compressed, the direction of the force within the material is the same as the direction of the external force. On the other hand, a compressed liquid transfers externally applied pressure uniformly in all directions throughout the liquid. Thus the pressure within a liquid body is the same, wherever measured. In our case an intermediate, viscous state is formed by small compressed particles, which are sintered together like a metal powder. When leather fibre particles are heated under pressure, their components soften to a certain extent. In this state the material behaves neither like a rigid material, nor like a liquid. It may, therefore, be expected that the pressure distribution in a die for such a material is similar to the curves as depicted in Fig. 3[3].

Due to friction between the fibres themselves and between the fibres and the confining walls, the local pressure inside the compressed material within the cylinder decreases with greater distance from the plunger and, directly under the plunger, increases with decreasing distance to the cylinder wall.

All of the above phenomena cause an unpredictable, non-uniform stress distribution during the production of Pleather and lead to the differing morphologies.

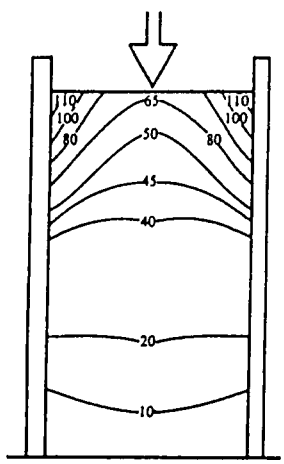


**Figure 3.** Schematic pressure distribution in a unidirectional compression of particles (from Ref.3).

## Experimental Results and their Interpretation, SEM micrographs*

A possible result of non-uniform stress distribution is shown on the micrograph of Fig. 2 at the left of the clearly visible void at (F/H,3/4). Here, due to too low a stress, the primitive fibres can not aggregate to form continuous material, but are merely split into fibrils. To the right of the void continuous material was formed, indicating sufficiently high local stresses. A void of this type could be formed when a fibre is pulled out of its surroundings as the result of compression during processing, and indeed, the size of the void is of the order of magnitude of the fibres.

## Stages of development

The right-angled manifestation of the structure of transformed material was discussed in reference 2. In Fig. 6 of reference 2 most of the particles are cubic, which phenomenon we ascribed to the action of mechanical forces. This phenomenon is exemplified in Fig. 2 by the right angled cavity at (A,3/4), where a squared particle has been dislodged. Fig. 4 shows a further developed stage, where under the influence of a processing pressure of 600 atm and a process temperature of 150°C for a process time of 9 min. the right angled particles assume rounded corners and are melted together. All these process parameters are higher than the processing values of the sample in Reference 2.

Whereas the cubic shapes are produced by mechanical forces, the round ones have a more natural appearance, as here the surface energy is minimized. Alternatively, a continuous structure is formed, as in Fig. 5 (processing parameters as in Fig. 4), some fibril debris is present, especially in the holes, where the pressure was low. The structure may also develop as seen in Fig. 6, where P = 300 atm, and T = 140°C, and time t = 20 min. The layered structure becomes leaf-like with corners that are rather rounded than squared.

* Photographed under a JEOL JSM—35C scanning electron microscope.

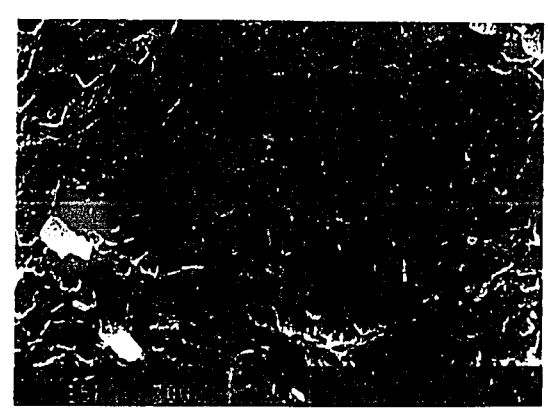

**Figure 4.** Geometrical particles with rounded corners, melted together. External process pressure: 600 atm, Temperature: 150°C, time: 9 minutes, Magnification: × 3000, Bar equals one hundredth of a millimetre ( = 10 μm).



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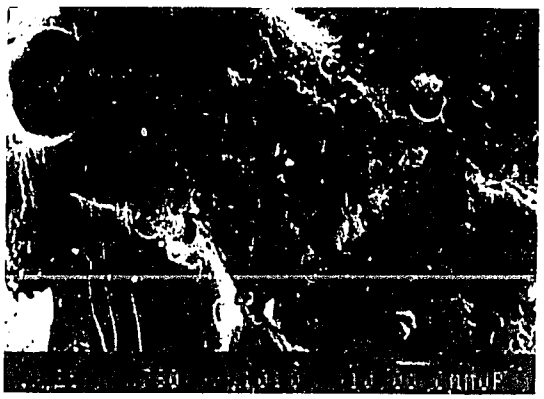

Figure 5. Continuous material, containing some fibril debris. External process pressure: 600 atm. Temperature: 150°C, time: 9 minutes. Magnification: × 780, Bar equals one hundredth of a millimetre (= 10 μm).

Figure 6. Leaf-like structure with rounded corners. External process pressure: 300 atm. Temperature: 140°C, time: 20 minutes. Magnification: × 1800. Bar equals one hundredth of a millimetre (= 10 μm).

## Compression at room temperature; heating at atmospheric pressure

Fig. 7 shows a micrograph of ground material that has been processed for 20 min. at room temperature at a pressure of P = 750 atm. In this case the original fibres have been compressed, only to become simply a thick bundle of fibres. No continuous material was formed.

On the other hand, we found that the supply of heat only, without compression, leads to carbonization of the leather fibre particles.

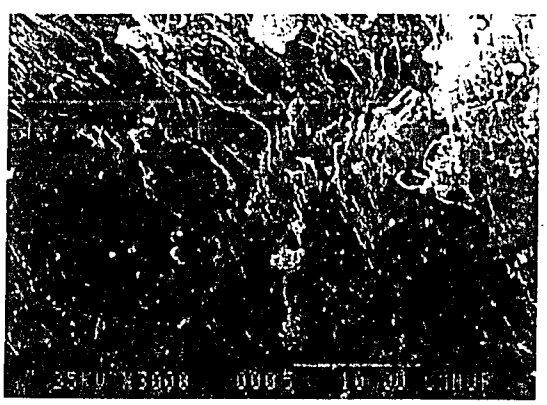

Figure 7. Ground leather, compressed at 750 atm for 20 minutes at room temperature, forming a thick bundle of fibres. Magnification: × 3000, Bar equals one hundredth of a millimetre (= 10 μm).

In this way it is shown that in order to initially break up the bonds between fibres and primitive fibres, and afterwards to produce the continuous material, the process must take place under both elevated pressure and temperature.

## Mechanical Properties, Compression Curves

In Fig. 8 we give the compression curves* of materials, made of mixed tanned bovine hide, as were measured at room temperature:

1—a piece of leather, curve A,
2—ground leather fibre, processed at P = 750 atm at room temperature, curve B,
3—ground leather fibre, processed at P = 650 atm and T = 85°C, curve C.

*Curve A* shows a normal compression curve of leather. (In order to obtain a test cylinder with a height of 8 mm two round pieces, each 4 mm high, were glued together). The relationship between the applied load, F, and the reduction of overall sample length, Δl, is not linear. The concave curve indicates that as Δl increases, a progressively larger force is necessary to further deform the material. The average value of compression yield strength for this kind of leather is 175 MPa. At a certain value of the compression load the inner structure of the material gives way. The resulting compression load decreases accordingly. A similar curve for a tensile load is described by Van Gulik and Klopper.[4]

*Curve B* represents the mechanical properties of moulded ground leather fibre, that has been compressed at 750 atm and at room temperature. The yield compression strength is 125 MPa, which is less than for leather.

*Curve C* was obtained by compressing hot pressed,

* All tests were performed on a Houndsfield, electrically driven bench. The test pieces had an initial diameter of 8 mm and an initial height of 8 mm.

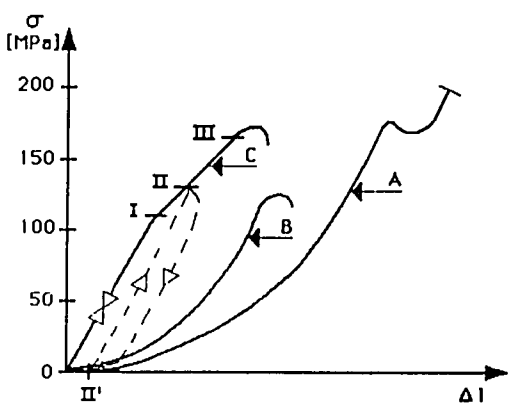


Figure 8. Compression curve of materials made of mixed tanned bovine hide:
Fig. 8A, a piece of leather;
Fig. 8B, ground leather, compressed at room temperature;
Fig. 8C hot pressed, ground leather, Pleather, processed at a pressure of 650 atm and a temperature of 85°C for 8 minutes.

ground leather fibre, processed at 650 atm and 85°C. The first part of the curve, between points O and I is linear and represents elastic deformation only. Each time the load on the specimen is relieved and re-applied from a randomly chosen point on the track between O—I, this part of the curve is re-traced. The second part of the compression curve, between points I and III is also linear. The kind of deformation that takes place in this region has been examined, too, by relieving and re-applying the load from point II, which lies between points I and III. The direction of the curve is as shown. We see that point II', reached after complete relaxation, does not coincide with the origin, meaning that deformation between I and III is partially plastic. The compression yield strength is 110 MPa, the compression break strength is 165 MPa. The stiffness of hot pressed, ground leather fibre is greater than that of both other materials examined. This can be seen from the initially steep slope of the curve. Young's modulus of compression for Pleather is of the same order of magnitude as that of nylon 6/6, $E = 3\text{-}4 \times 10^9$ Pa.

## Conclusions

1. Depending on pressure, temperature, and time during processing, there are many variations of the microscopic morphology of hot pressed, ground leather. These vary from continuous material to continuous material with fibres, and layered material, either squared or rounded.
2. The external pressure is not an unequivocal parameter, as there are unpredictable voids in the material and as stress distribution is never uniform in a viscous mass that is being unidirectionally compressed.
3. It is essential that, besides the pressure which provides the mechanical energy to split the fibres and the primitive fibres, there is enough thermal energy available in order to enable the continuous phase to be formed.
4. Hot pressed, ground leather shows a compression–strain curve that is different from that of leather. Its curve resembles that of metals, as it shows distinctly elastic and plastic parts. Its compression stiffness is of the same order of magnitude as that of nylon.

## Acknowledgements

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ty to react appropriately and come up fast with the right solutions.

The French social scientist Jean Fourastié used a very apt description of this situation some time ago when he stated that in the space of ten years the present-day entrepreneur faces problems on three occasions which his father and grandfather had a lifetime to solve. And he is by no means the only person to consider that the conventional three-point profile of demands remains behind the real requirements of the future. Thus the chairman of Daimler-Benz, Edzard Reuter stated that there will be a future need for many more people having a broad knowledge and broad experience in the field of general management, abbreviated as general managers, in addition to the many indispensable specialists.

The ability to cast a look over the fence, the skill of grasping not only the overriding relationships but above all also complex and uncertain ones, is rapidly advancing to become one of the decisive professional qualifications.

Ewald Kock (proprietor of Personal Marketing Ewald Kock Training in Hagen, Westphalia) summarises the situation by stating that most people do not think in a manner appropriate to today. They think too slowly and in conventional and at least semi-obsolete terms. When the good old Swiss watch had been pronounced clinically dead, Swatch appeared and demonstrated that the dead can rise again. The Walkman, now an almost universal phenomenon, demonstrates how a conventional old product, viz. the tape recorder, can recapture its youth. Only because an elderly Japanese gentleman refused to think in the fetters of conventionality: the future will be won in the mind! Only in the mind. This will be the crucial factor in tomorrow's economic and social life: releasing the thought processes from old patterns.

The internal stability of companies–and also of people–results from the acceptance of the necessity of the co-existence of constancy and change, of continuity and flexibility, of concentration and relaxation, as the Swiss management consultant Edmond Tondeur once stated. However, people and companies can only derive true assurance in the face of the future from their internal vitality. Only for the intellectually open, venturesome person does the future cease to be a threat but instead a source of rich opportunity.

Existence-threatening thinking, managing one's life as an intellectual one-way street, has to be replaced by what Harvard Professor Ellen Jane Langer aptly calls mindfulness. In contrast to the restricted thinking lacking in perspective, which is seen by the careful observer wherever he or she goes, mindfulness has been convincingly demonstrated in numerous studies to release great potential.

In our present society whose knowledge is growing by roughly 5 % per year, and doubles every 10 to 15 years at the latest (for the sake of comparison: it took a whole century for human encyclopaedic knowledge to double between the years 1800 and 1900 and it still took half a century for the next doubling to take place between 1900 and 1950) mindfulness is absolutely essential.

In addition, there is an impressive body of evidence that psychic factors play a dominant role in the origin and course of most diseases. Changes in the immune system play a decisive role in this context. The human immune system is profoundly influenced by the way in which a person thinks.

Not only victory and defeat on the sports field but also matters of health are decided in the mind. Or in the minds–of the employees–in the case of the health of a company.

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# Microscopical Observations on Pleather

**A new Thermoplastic Material made of Scrap of Leather or Hides**

*by Dr. A. Wyler, Dipl. Ing. R.T. Markus, Jerusalem College of Technology, Jerusalem, Israel, and Professor Dr. B. de Castro, Faculdado de Ciencias, University of Porto, Portugal*

A new approach is being developed to reprocess scrap of leather and hides. This process is based on heating and compressing their fibers and produces a material with thermoplastic properties. Because it is made from leather and also has thermoplastic properties, the term Pleather has been coined, to designate the new material. The internal structure of Pleather is dependent from the process parameters. After complete transition the material does not bear any more structural resemblance to leather. Pleather may be made into many intricate shapes through plastic forming techniques, as injection molding, or compression molding. It may even be recycled, much the same as scrap of other thermoplastic materials.

## Introduction

The internal structure of skin or leather can be changed through the application of heat and pressure for a predetermined time. The outcome of this process is a complete change of chemical and mechanical properties of the collagen. The resulting material is Pleather. Chemical tests showed that the average chain length of the new material is much smaller than that of the leather used, mixed tanned bovine hide.

Mechanical properties were examined too, and showed how, dependent on the process parameters, properties change. In this article we will also discuss the advantages of thermoplastic Pleather as an industrial material.

## Production of Samples

By comminuting pieces of mixed tanned bovine hide in a Wiley mill the leather is reduced to fibers, the raw material for the process. Fiber length is approximately 5 mm.

To produce Pleather the fibers are compressed and heated in a mold for a preset time. Heating takes place electrically, cooling by means of a water cooled coil. Process temperatures are over 70 °C. The applied process pressure may reach values of a few hundred bars.

Preparation of samples for analysis by means of a SEM includes cleavage of the specimen and sputtering of gold in order to coat its surface with a 200 A layer to make it

[illegible] The SEM used is a JEOL JSM-350 scanning electron microscope.

## Results

### Stereo Zoom Microscope

The transition from fibers of mixed tanned hide to Pleather may be devided into several stages, as observed through a stereo zoom microscope at a magnification of X 30. In the first stage, produced at P = 250 atm and T = 100 °C, fibers undergo transition to Pleather and stick together (fig. 1). In the second stage these particles lose their fibrous character and form the continuous material, Pleather (fig. 2) produced at P = 450 atm and T = 160 °C.

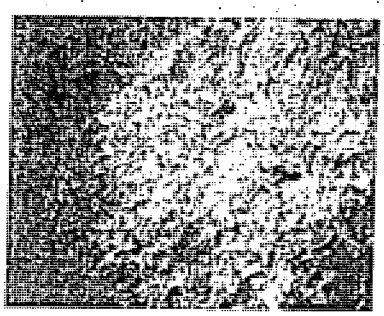

Fig. 1: Joined leather fibers, processed at 250 atm and 110 °C, in the first stage of transition to Pleather, magnification = X 30

### Scanning Electron Microscope

Pictures were taken with a SEM in order to investigate the structure at a scale, two orders of magnitude smaller than possible with an optical microscope. As can be seen from figures 3 and 4 the process causes a radical change of the internal structure.

Fig. 3 shows some primitive fibers with a diameter of between 2.5 and 5 µm, protruding from the continuous Pleather structure. Process pressure P was 50 atm and process temperature T = 155 °C. The fibers in the picture are made of either as yet unmodified

Fig. 2: The final stage of transition from leather fibers to continuous material, Pleather, processed at P = 450 atm and T = 160 °C. The original, fibrous character disappeared, magnification = X 30.

Fig. 3: SEM Micrograph of continuous material, Pleather. Protruding are either unmodified fibers (diameter: 2.5 to 5 µm), or elastin fibers. The cross-sectional shape is rectangular, temperature = 155 °C, magnification = X 50.

collagen – this may be caused by a locally, insufficiently high pressure – or exist as elastin, a more difficult to modify polypeptide. At a magnification of X 550 the tips of the fibers are shown to have a right angled cross-sectional shape. This was caused by the externally exerted pressure.

The structure in fig. 4 shows material that was processed at the same process pressure as the previous specimen, P = 50 atm, but at a much lower process temperature, T = 110 °C. The larger magnification X 6600 reveals at the fibrils of which each fiber con-

Fig. 4: SEM Micrograph, successive phases of the transformation from leather fibers to the continuous material, Pleather. Fibers (diameter: 1 µm), consisting of primitive fibers (diameter: = 0.1 – 0.5 µm), flaky material, cubes and continuous material, pressure = 50 atm, temperature = 110 °C, magnification = X 6600.

[illegible] than 0.5 µm. The transition from fibrous to continuous material can be observed, much the same as in fig. 2. More to the left the continuous material has reached its final phase, under the prevalent process parameters, and seems to consist of fused, regularly shaped particles, all having right angles.

### Change in Chemical Structure

With a progressing degree of transformation of the original material the solubility of Pleather samples in dimethylsulfoxide $(CH_3)_2SO$ increases and the amount of material that is extracted by the Soxhlet method, goes up too. Samples with total transformation of leather fibers to Pleather were completely soluble. These observations strongly suggest a breakdown of the three-dimensional network of collagen in Pleather and a transformation process that reduces the average molecular weight of the collagen clusters, possibly through cleavage of the polypeptide chains. The transition of leather to Pleather is accelerated by increasing the internal energy through the supply of heat. Ground leather, which has an average molecular weight of 300.000, (ref. 1), is hardly soluble at all in dimethylsulfoxide.

### Mechanical Properties

As may be expected of a material with a structure so different from that of leather, the mechanical properties of Pleather differ greatly from those of leather. Hardness measurements were performed with a Shore D meter and are based on the depth of impression of a sharp needle into sample material. In order to accurately measure the hardness of a sample, its thickness must be at least ten times the depth of the impression or else the hardness of the background

| Breakdown | Assumptions | Cost per Annum (DM) |
|---|---|---|
| Labor | A team of 2 unskilled laborers 45 h/week · 48 weeks per yr, 2160 h/yr at DM 10/h | 43,200.– |
| Raw Material | 60 kg/h: 130 ton/y · Pf 20/kg | 26,000.– |
| Chemicals | DM 1/kg · 20 kg/h · 2160 h/yr | 43,200.– |
| Equipment | DM 660.000.– for three presses (200 ton) plus dies, grinder, heating, and aux.<br>20 % depreciation/yr<br>10 % maintenance 40 %<br>10 % interest | 264,000.– |
| Energy (electricity) | 50 kW<br>Pf 20/kWh · 2160 h/yr | 21,600.– |
| Occupancy | No special requirements, 50 $m^2$ | 2,000.– |
| Overhead & Supervision | 20 % of labor cost | 8,600.– |
| Financing | 1 % Labor cost<br>6 % Chemicals<br>1 % Occupancy etc. | 2,600.– |
| **Total cost per year** | | **DM 411,200.–** |

will influence the results. Therefore, for the measurement of leather, several pieces were placed upon each other. Pleather samples may be produced in thicknesses that exceed by far the maximum thickness of leather, which is limited by nature. As the process temperature and pressure increase, the hardness of the material increases from approximately 50 to 85 Shore D, versus an average of 55 Shore D for the leather used by us.

The compression yield strength depends on the process parameters and ranges at room temperature between 50 and 185 MPa, which equals or even exceeds that of 20 % glass-fiber reinforced nylon which has values of between 160 and 180 MPa. (ref. 2)

## Economic aspects of Pleather

The production process of Pleather is suitable for automation as well as unskilled labour. This process therefore, can be applied in both the industrialized as well as third world countries where it may be a captive industry, located next to leather processing factories or slaughterhouses.

The following, rough price calculation is made for a product of 100 g, made of Pleather. This calculation does not take into account shipping costs, marketing costs etc.

Without going into technical details it may be assumed that with the above mentioned equipment it is possible to produce 1.3 million items per year, e.g., footwear, luxurious packaging, etc. This results in a retail price ranging from approximately DM 0.30 per piece in developing countries to DM 0.45 per piece in industrial countries, where labour costs and accomodation are more expensive, indicating a reasonable price of product.

Prices of scrap material are expected to rise once Pleather will be produced on a large, industrial scale. On the other hand research is expected to lead to improved and cheaper production methods, and also to better properties of Pleather, making it a cheap replacement of leather. The price of raw material for Pleather would approximately lie between DM 0.60 – 1.50 per kg, which is to be compared to DM 9 – 18 per kg for real leather.

## Characteristics of Pleather

Unlike the classical leather industry, where automation is difficult because of the variable quality and dimensions of the raw material, Pleather procution may be automated as in the plastics industry. Pleather articles may be produced in many intricate shapes, in one production step only.

Countries with bountiful sources of scrap of hides and of leather can reduce their dependence of petrochemical-based raw materials, the prices of which are subject to unpredictable fluctuations.

In "1985 World Prognosis", a need for 9 billion pairs of shoes is predicted for the year 1990. Conventional sources of leather can provide only for 6 billion pairs. It is generally believed therefore, that the volume of plastic shoe sales (PVC, polyurethane) will grow drastically until the end of this century. When the properties of Pleather will have been successfully optimized, Pleather could be used for molding whole shoes, or parts of them at competitive costs. Furthermore, there exists a possibility of using Pleather as a replacement of leather in all objects where the "breathing" property of leather is not critical. Objects could be produced by relatively cheap, conventional, plasticforming techniques. Furthermore, Pleather may also be used under conditions incompatible with most thermoplastic materials, e.g. at cryogenic temperatures or under ultraviolet radiation, as in sunshine.

## Discussion and conclusions

In a newly developed process the basic properties of leather are changed to produce Pleather, a thermoplastic material. As shown before, non-uniform pressure and temperature distribution throughout the material during the process leads to different phases within the specimen.

Pleather is an answer to the problem of scrap of tanned and untanned hides and skins. It may be used in different applications, under working conditions that cause properties of other thermoplastic materials to deteriorate. Microscopic examination shows Pleather to have a completely different structure from leather, due to the breaking down of the molecular structure.


### Acknowledgements

The help of Mr. Carlos Sa from the Department of Electron Microscopy at the University of Porto with the SEM work is gratefully acknowledged.

We wish to express our gratitude to Mr. Yehuda Frankl, Head of the Leather Department of the Israel Fibers Institute, for useful discussions.

This research is financially supported by the Cooperative Development Research Program of the Agency for International Development in Washington DC, USA.


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## 'inishing of Leather Soles

ormally, the edges of leather soles are noothed off and brought to a high polish ith a rotating disk after waxing. However, is is not always the best approach. Somenes, e.g. in the case of the edges of xible sandals, this operation is better permed with a buffing wheel made up of lividual pieces of leather.

## lp in Lasting

work of the sandal laster and the pulling r operation can be greatly facilitated by king not only the length of the vamp but the centre line on the last. Correct ntation of the uppers is then simple.

## Application of Leather Filler

Some black and dark blue leathers have a better sheen and feel if they are treated twice with leather filler.

## Lasting Aid for Multistrap Sandals

Multistrap sandals can generally be lasted better if the individual parts are first positioned on a corresponding pattern, a small strip is attached along the lasting allowance, and a seam stitched along this strip. After lasting the strip is removed in connection with the roughing operations.

## Smaller Girth for Multistrap Sandals

The multistrap sandals so popular in summer have a tendency to stretch fairly quickly, even if the straps have reinforcing tapes. It is therefore recommended that such shoes be produced on lasts of somewhat smaller girth.

## Making Elasticized Boots

The uppers of elasticized boots should stretch at the heel by some 40 % to facilitate an easy get-through, though a stretch of only 7½ % is required at the edge of the upper.

# A NEW CLASS OF COMPOSITE MATERIALS:
# MATRIX AUTO-REINFORCED ORGANIC MATERIAL - MARIOM

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A sort of composite materials can be produced from a single kind of natural organic fibers. This has been observed with bovine leather. During the formation process in a die particulated leather fibers were subjected for a period of about six minutes to a pressure of over 100 bar at a processing temperature of between 60 and 200 °C. In this way a portion of these collagenous fibers was plastically deformed and converted into continuous matrix material in which unconverted fibers act as matrix reinforcement. Round, collagenous fibers assumed an angular cross-section and became the building blocks of the continuous matrix. This is clearly visible on pictures made with a scanning electron microscope.

At a processing temperature of 70 °C and a pressure of 650 bar, applied for six minutes, the maximum compression strength at room temparature is found to be 185 MPa. At these processing parameters Young's Modulus is about 2.4 GPa, the apparent density is 1350 $kg/m^3$.

Other natural fibers, to be used as organic raw material for the production of composites, are currently under investigation.

A new class of composite materials was produced when the matrix and the reinforcing fibers, were formed from the same starting material. A lightweight, polymeric composite material of good strength was obtained by heating and compressing fibrous, organic material in a die.

The new composites are designated MARIOM: Matrix Auto-ReInforced Organic Material. MARIOM's phases consist of:

a. matrix: continuous, polymeric material, formed from converted fibers, and
b. reinforcement: fibers of the same kind, that are not converted at all or just partially.

To demonstrate this kind of "in-situ" conversion of fibers into a composite material, we used comminuted scrap of leather.

Leather, as seen with a scanning electron microscope, (fig. 1), consists of fibers with a rounded cross-section and a diameter of about 5 µm. A fiber is built of so-called primitive fibers that have a rounded cross-sectional diameter of about 1 µm. These in turn are composed of fibrils with a diameter of about 0.1 µm.

We found that fibers get loose when heat was applied at temperatures between 70 - 200 °C and pressure was exerted at over 100 bar. Pressure within a compressed, particulate material in a die is distributed in a non-uniform way. (ref.1) Therefore, only in those places where the pressure is sufficiently high, fibers undergo plastic deformation. In these locations the cross-sections of the primitive fibers become

flattened, or tri- or quadrangular. Whilst round shapes cannot totally fill the space, flat primitive fibers and tri- and quadrangular ones can and do. This enables deformed primitive fibers to fuse in an optimal way and form a continuous material. (reference 2 elaborates on the morphology of the internal structure of MARIOM)

Fig. 2 shows a SEM micrograph of a MARIOM composite as produced from ground leather particles. The micrograph clearly shows both phases of MARIOM, the continuous matrix and the embedded, angular reinforcing fibers. In this figure locations are indicated by means of coordinates next to the micrograph, e.g. (3,D), whereby an area is indicated by e.g. (3/5,A/D). At (1/3,G/J) angular particles are found. At (5/7,A/E) and (2,H) plastically deformed primitive fibers are seen to fuse, the process during which continuous matrix material is held to be formed. In a further stage, seen at (5,C/E) and (1/2,E), fusing primitive fibers merge with already formed continuous matrix material.

At continued processing ever more deformed primitive fibers are converted into the continuous matrix material through a yet unknown mechanism.

It is possible to vary the strength of the material by changing the processing parameters. In this way we regulated the ratio of unconverted to converted primitive fibers in the matrix. Fig. 3 shows a curve of the compression strength of collagenous MARIOM, measured at room temperature, as a function of the processing temperature. With all measurements the processing pressure was kept constant at 650 bar for six minutes. Up to 60 °C only unconverted, compressed leather particles were

found, the intrinsic compression strength of which is 145 MPa. At the prevailing processing pressure and temperature the compression strength reached a maximum value of approximately 185 MPa at a processing temperature of 70 °C. However, as the processing temperature is raised, an ever increasing number of primitive fibers converted within the given processing time. At 130 °C almost all leather particles were converted and only the weak continuous matrix material remained. The strengthening mechanism of MARIOM is the subject of current research.

The maximum obtained value of 185 MPa for the compression break-strength is in excess of that of nylon reinforced with 20% glass fibers.

At the same processing parameters that produce this maximum compression break-strength, the value of 2.4 GPa was obtained for the stiffness of the composite, as expressed by Young's modulus. This is higher than that of nylon 6/6. The apparent density, as mentioned, was 1350 $kg/m^{3:}$. The average apparent density of leather, the raw material, was about 900 $kg/m^{3:}$.

We observed that processing temperatures of between 70 and 90 °C and processing pressures of over one hundred bar, as applied in the conversion of collagenous material into the new MARIOM composites, insure its mechanical properties remain stable when used at room temperature and at moderate pressures. This phenomenon may be compared to the artificial precipitation hardening at 150 to 200 °C of Duraluminum alloys that retain their strength during their entire life-span when exposed to

temperatures lower than their hardening temperature.

The importance of the development of this new composite is that both matrix and reinforcment are produced from the same inexpensive raw material. The raw material is leather or other fibrous material, typically of a natural origin, widely available, and not a petroleum derivative. MARIOM may be biodegradable and, therefore, "ecologically friendly".

For the selection of potentially usable natural fibers much attention should be paid to the properties of the fibers at processing, their properties as reinforcement and topological considerations of filling space.

We may conclude that:

1. A new class of composite materials can be devised whereby both matrix and fibrous reinforcement derive from the same, natural raw material.
2. By judiciously choosing the process parameters it is possible to optimize the values of certain mechanical properties.

Keywords:

Natural fiber, composite material, matrix auto-reinforced organic material.

Acknowledgements:

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## Figure Legends

Fig. 1: Bovine leather. The fibers have an average diameter of 5 µm and are built up of primitive fibers with an average diameter of about 1 µm. Magnification: X 1500. The length of the white bar represents 10 µm.

Fig. 2: Tri - and quadrangularly shaped, converted primitive fibers are embedded in a continuous matrix. Both particles and matrix are produced from converted primitive fibers of leather. External processing pressure: 300 bar, processing temperature: 140 °C, Processing time: 6 minutes. Magnification: X 5400. The length of the white bar equals 1 µm.

Fig. 3: Compression strength of MARIOM at room temperature as a function of the processing temperature. Processing pressure: 650 bar, processing time: 6 minutes. The bars represent the spread of five measured values.

Fig. 1: Bovine leather. The fibers have an average diameter of 5 µm and are built up of primitive fibers with an average diameter of bout 1 µm.
Magnification: X 1500. The length of the white bar represents 10 µm.



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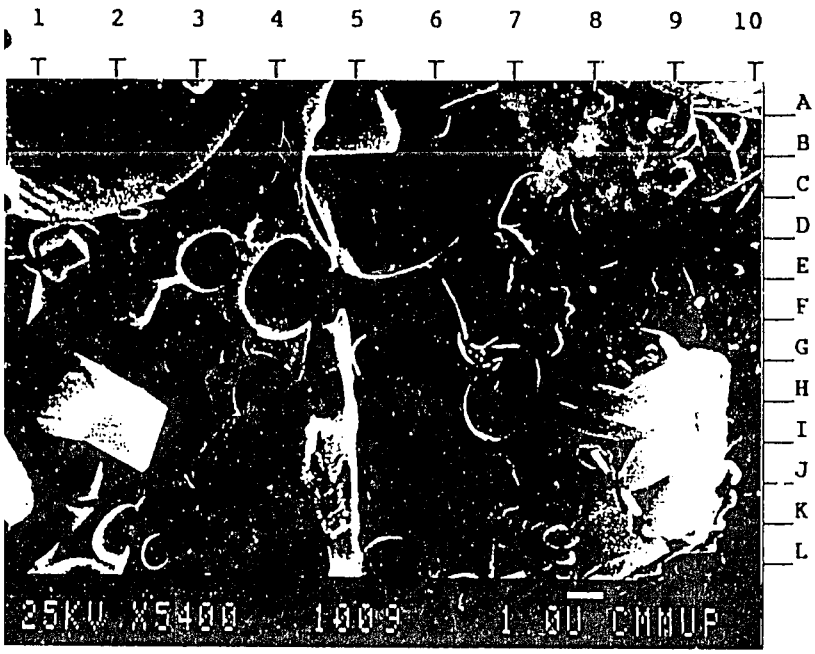


Fig. 2: Tri - and quadrangularly shaped, converted primitive fibers are embedded in a continuous matrix. Both particles and matrix are produced from converted primitive fibers of leather. External processing pressure: 300 bar, processing temperature: 140 °C, processing time: 6 minutes.
Magnification: X 5400. The length of the white bar equals 1 µm.



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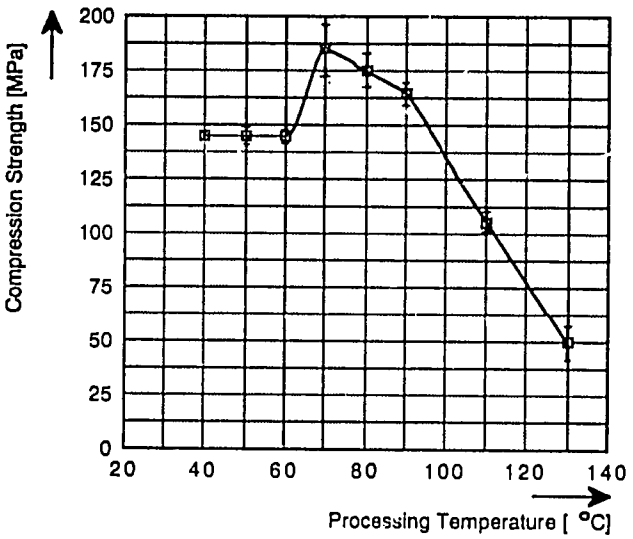
Compression Strength [MPa]
200
175
150
125
100
75
50
25
0
20
40
60
80
100
120
140
Processing Temperature [ °C]

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Short Title: "Fusion Bonding of Leather Parts"

# A Microscopic View of the Fusion Bonding of Vegetable Tanned Leather Parts

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## 1. Introduction:

In our research on the bonding mechanism between parts of leather we try to develop a method for welding of leather. Elsewhere (ref. 1) we have reported that by applying pressure and heat to two parts of leather which are in contact with each other, a strong bond is formed.

By pulling the parts from each other by pure shear, we have found that the bonding is about twice as strong as the bond that exists after gluing the two parts together with any of the conventional glues used in the leather industry.

Here we report our conclusions about the underlying mechanism of the bonding as determined by scanning electron microscopic observations of the bonded surfaces.

## 2. Theory of fusion bonding of organic material:

The theory of the welding of two parts made of linear polymers (thermoplastics) is well established (see for example ref. 2). The general picture is that small and thin chains of one part are able to inter-diffuse and penetrate into the opposite polymer side under the influence of heat. A relatively strong bonding comes into being, partly by the mechanical interlocking, and partly by the chemical (electrostatic) bonding forces between the thin inter-

penetrating chains into the network of the opposite polymer part.

In the case of leather the situation is more complicated than with the linear chains of a simple thermoplastic material, because of the crosslinking and interlacing of leather fibres. With respect to the problem of how to weld leather parts together, there are two differences when we compare welded leather to the simple structure of a thermoplastic.

1. In leather there is an intricate three-dimensional network of fibre bundles, compared to the simpler long linear chains of the thermoplastic material.

2. The diameter of the fibres in leather is about 5-10μm (Fig. 2) as opposed to the thin chains with a diameter of maximum 0.01 μm in thermoplastics. Long, thin chains of plastic are able to diffuse into the opposite plastic part under the influence of heat. Thick leather fibre bundles are not mobile enough to perform this inter-diffusion. However, the fibre bundles are composed of primitive fibres with a diameter of about 1μm, and these primitive fibres are built up from fibrils with a diameter of 0.1μm. There is a way to split the fibre bundles into their constituents: by applying heat and pressure together it is possible to split the fibre bundles into their more elementary components. The relatively thin primitive fibres, and certainly the thin fibrils, are able to attain enough energy from the heat and the mechanical pressure to diffuse into the opposite leather part. The fusion welding occurs now in two stages: (i) Pressure and heat together loosen the fibre bundles, and in

that way the primitive fibres and fibrils free themselves out of the fibre bundle. (ii) It is also this pressure which presses the primitive fibres and fibrils, that are mobile at high temperature, into the opposite leather part, where they interlock mechanically with the available primitive fibres and fibrils in the opposite side. The strongest bonding comes into being when there is also a strong electrostatic bonding between the interlocking fibrils of the opposite leather parts.

## 3. Experimental Methods and Results:

### 3.1. Fusion welding and shear tests.

Two parts of vegetable tanned bovine hides with a thickness of 4mm were cleaned with air at high pressure and put one on top of the other. Afterwards a high mechanical pressure of P=450 bar was applied for 4 min during which the temperature was raised from room temperature up to T=115° C. After being held at the maximum temperature for 4 mins, the two parts were cooled by a waterflow underneath their metal support.

Afterwards the two parts were separated by shear forces applied to the bond by a Houndsfield electrically driven tensile machine. The strength of the bond varied between 40 and 60 kg/cm² as measured on 15 samples.

### 3.2. Observations with a Scanning Electron Microscope:

In order to be able to look at the welded samples the surfaces were sputtered with a 200 A gold layer and the samples were investigated in a SEM. Figures 3a and 3b show



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the seam between welded leather parts. The magnification in Fig. 3a is about 18X and in Fig. 3b, 900X. The thin primitive fibres and fibrils that are able to bridge over the "abyss" between the two parts and to form a bonding by inter-penetration in the opposite leather network are visible in a direct way in micrograph 3b, where the parts have been separated slightly for clarity. Observations on the welded parts after they had been torn from the opposite side showed the presence of a majority of primitive fibres and fibrils, compared to the thick fibres in plain leather in Fig. 2. Although this is an indication that the above described mechanism is probably correct, formally it is not proof, because the fibres could have split during the shearing tests.

## 4. Discussion and Conclusions:

The mechanism of inter-fibre diffusion as a bonding mechanism for leather has been established by the electron microscopic picture in Fig. 3.

In our view this fusion welding mechanism includes two steps:

1. The splitting of thick fibre bundles in primitive fibres and fibrils under application of high pressure and moderate temperature.

2. The inter-diffusion of these thin primitive fibres and fibrils into the opposite leather network where a mechanical interlocking of the fibrils comes into being. Experimentally we have found that the shear strength of the bond is of the order of magnitude of 50 $kg/cm^2$.



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The strength of the bond is probably only partially determined by the mechanical interlocking. The electrostatic (chemical) bonding between the molecules themselves are presumably the determining factor for the strength, but that has not yet been proven.

The difference between the bonding mechanism by fusion welding which is herein described, and which is based on a physical process, and the common method of adhesive bonding, is two-fold:

a. In the bonding by gluing of leather parts it is the glue that interpenetrates into the leather network making a short range electrostatic bonding as opposed to our longer range fibrillous bonding. This is also the reason that the shear strength of glued parts is maximum 25-30 kg/cm² compared to 50 kg/cm² by the welding process--this is almost 100% more!

b. The glue is an agent of distinctive completely different properties, i.e. foreign. The inherent strength of the glue itself is a limiting factor for certain adhesive types of bonding. In addition, glues tend to come unstuck in time and their bonding strength tends to deteriorate.

The strength of the bond formed by fusion welding is always lower than the strength of the leather itself because of the fact that the regular fibrous network that gives leather its strength has been partly destroyed and replaced by a random interlocked network of the primitive fibres and fibrils.



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Acknowledgment:

Thanks are due to Mr. Carlos Sa from the Department of Electron Microscopy at the University of Porto for the SEM micrographs and to Mr. J. Shulman, B.Sc., for help with the mechanical tests.

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Short Title: "Fusion Bonding of Leather Parts"

Captions: belonging to: A Microscopic View of the Fusion Bonding of Vegetable Tanned Leather Parts

Fig. 1. Partial inter-diffusion (black lines) of polymer chains

Fig. 2. Vegetable tanned leather--fibres (5-10μm), primitive fibres (~1μm) and fibrils (~0.1 μm)

Fig. 3a. Welded seam between two fusion bonded parts. Magnification 18X.

Fig. 3b. Detail of Fig. 3a. Magnification 900X.

xg10/fibrils2.wyl

Lifelines:

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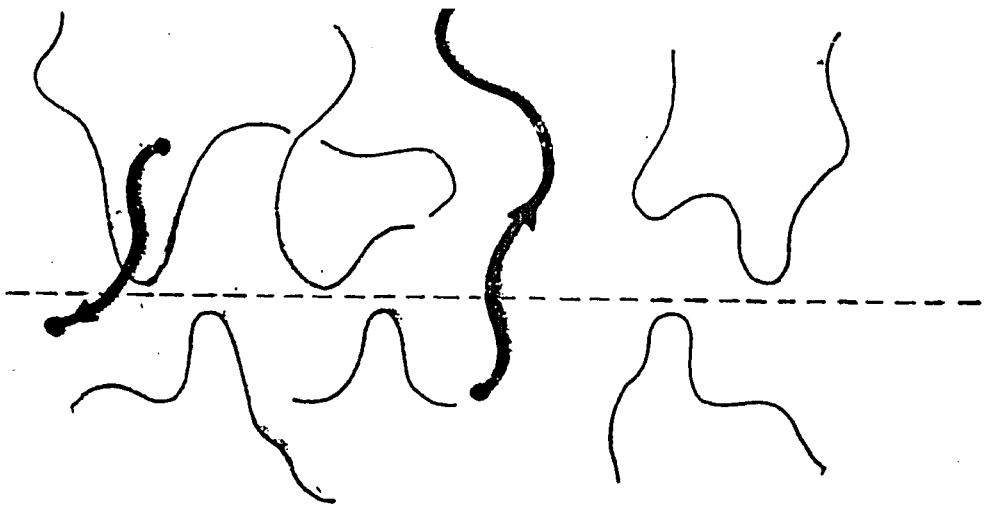


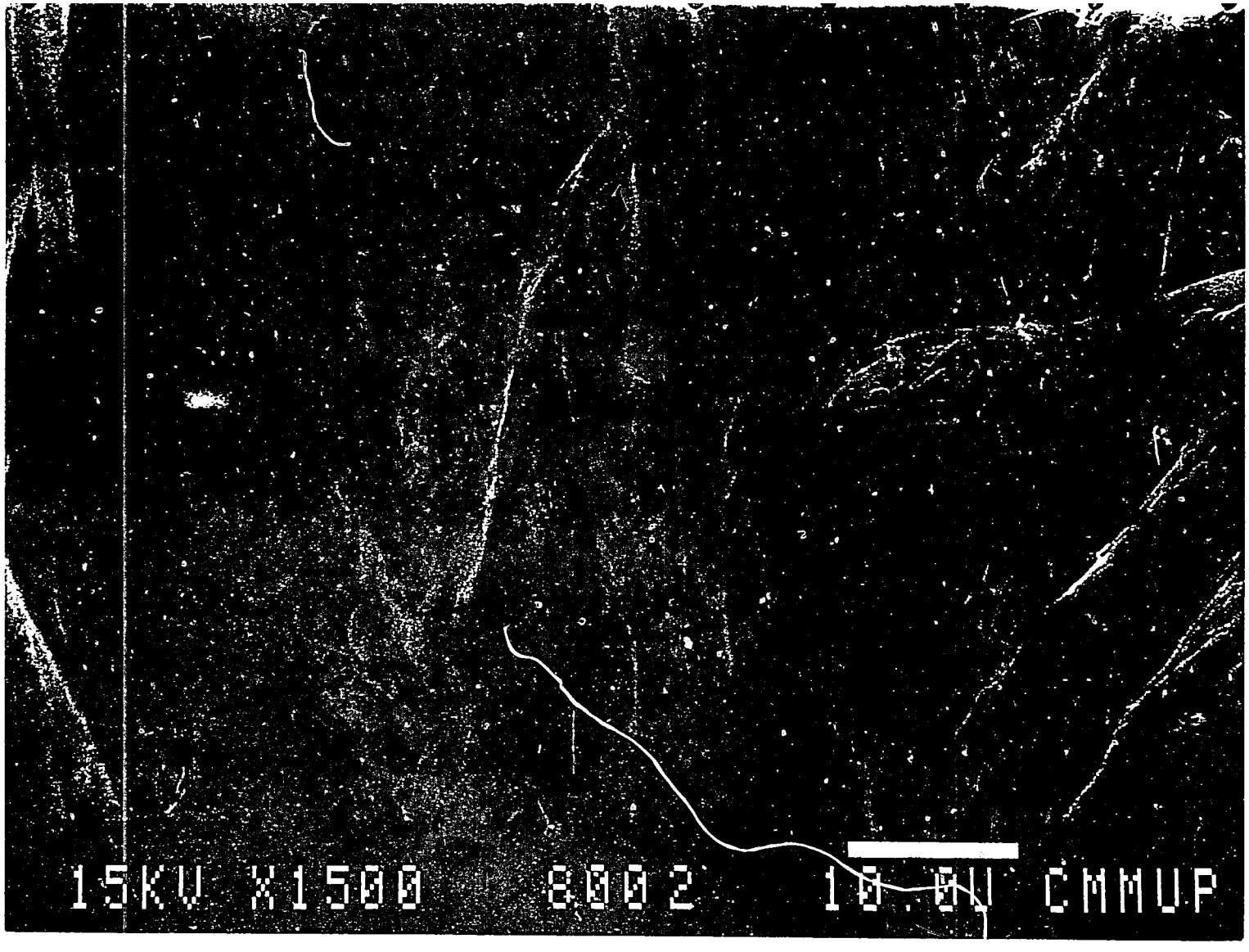



Fig 2

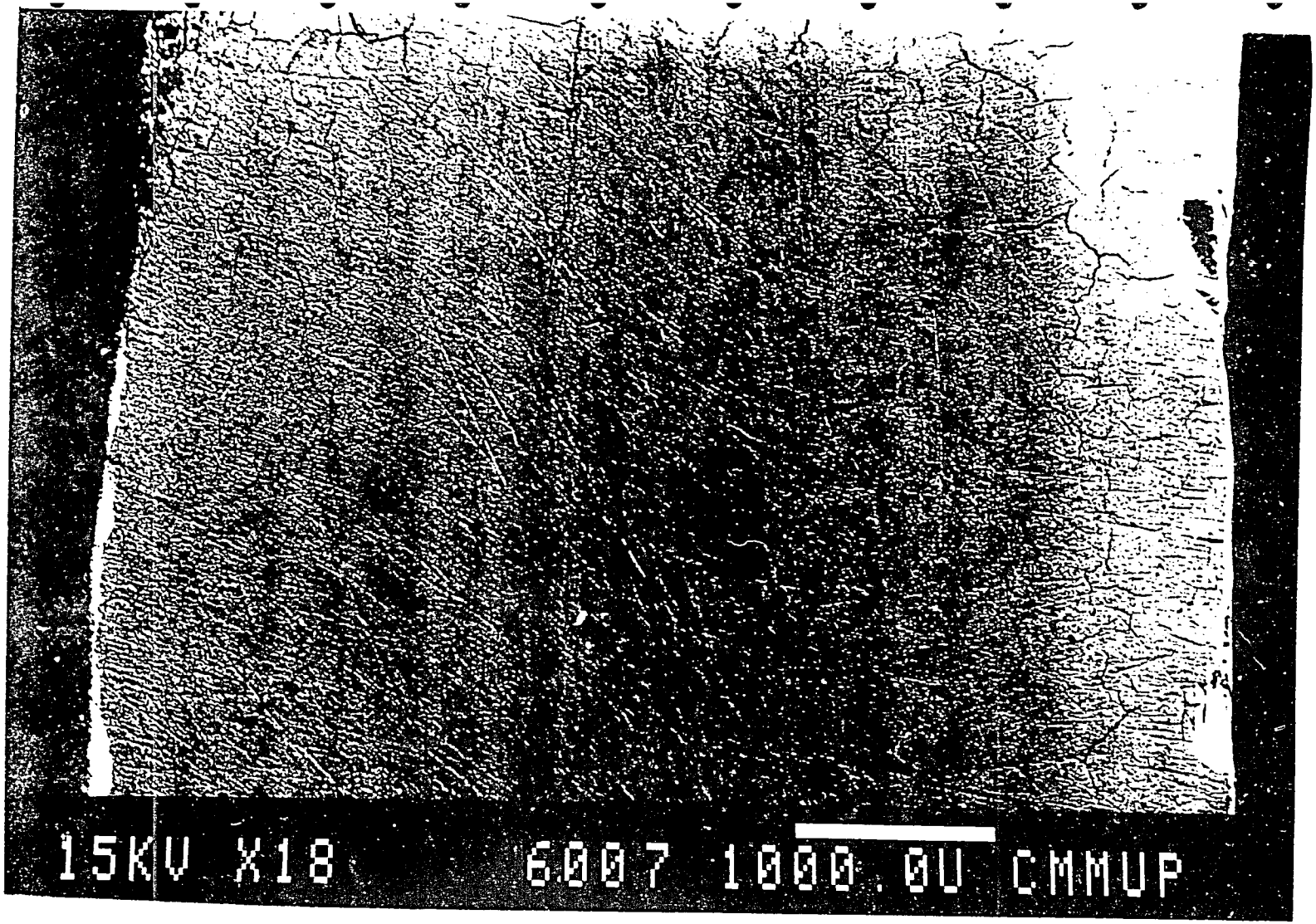
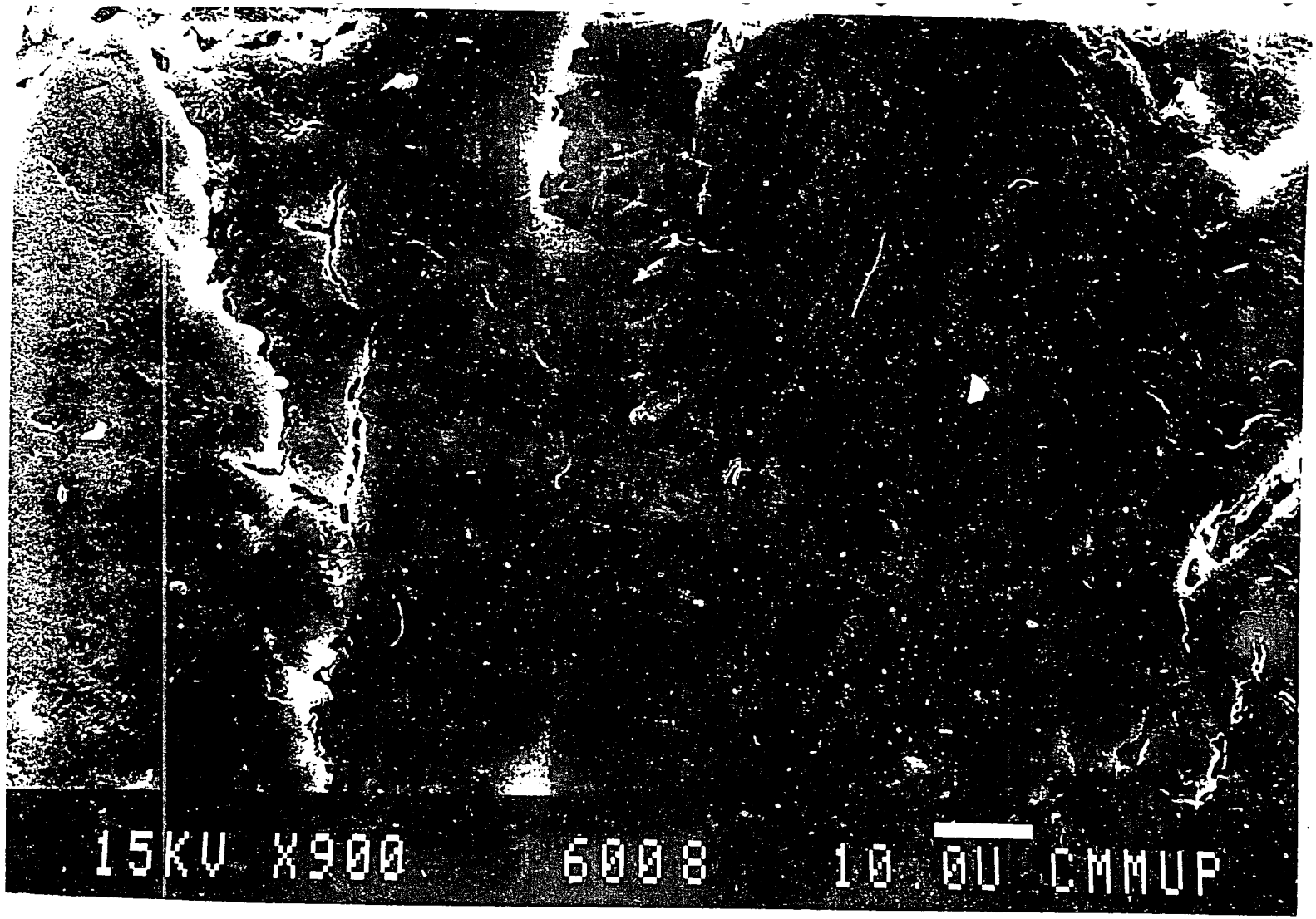



Fig 3a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FINAL REPORT

of the Portuguese Participation on the thermoplastic leather, PLEATHER Project

Grant No. AID-C5-268

Program in Science nd Technology Cooperation

U. S. Agency for International Development

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In this report only the following items are covered :

5 METHODS AND RESULTS

6 IMPACT, RELEVANCE AND TECHNOLOGY TRANSFER

7 PROJECT ACTIVITIES/ OUTPUTS

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# 5 METHODS AND RESULTS

Draft of publication number 7 on next page

When leather is heated at elevated pressures a new material exhibiting thermoplastic behavior is obtained – *pleather*. During this process no amino acid destruction was observed, since amino acid analysis of leather and of *pleather* lead to the same composition before and after transformation, thus implying that the physical transformations observed must be associated with a break down of the collagen superstructure in tanned leather.

The key aspect of the portuguese participation was to determine directly the microstructure and to gain insight into the molecular structure of the transformed leather, and thus to be able to relate the properties of the new material ( *pleather* ) with changes in the structure of leather and of the associated collagen network.

The other goal of the portuguese participation was to achieve a significant chromium removal from leather and to assess the properties of the transformed material.

This section is divided in three subsections that reflect the different methodological approaches used: the first comprises the microstructure studies using ~~TEM and~~ SEM; the



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second the studies involving molecular weight assessments of the collagen fragments in leather and in *pleather*; and the third describes the methodology used in chromium removal.

## 5.1 MICROSTRUCTURE DETERMINATIONS

# # I will leave this section to the JCT team. # #

## 5.2 STRUCTURAL CHARACTERIZATION OF PLEATHER

Leather has an extended network of collagen fibers that is insoluble in almost all solvents. This insolubility is due to an extensive cross-linking between the collagen fibers that results in assemblies of huge molecular weight. The partial solubility of *pleather* in dimethylsulfoxide (*dmso* ) and in buffer solution used in biology is then attributed to a breakdown of the collagen superstructure induced by the thermal treatment at high pressures, since only lower molecular weight fragments can be solubilized in these solvents. We were able to correlate the processing temperature and pressure with the solubility of the resulting *pleather*, and also the solubility in buffer solution with the molecular weight of the soluble fragments.

### 5.2.1 SOLUBILITY MEASUREMENTS

Draft of Publication no 7.

#### MATERIALS AND METHODS

LEATHER PROCESSING. Hot pressed leather ( *pleather* ) was obtained from leather comminuted in a Wiley mill that was subsequently heated in a hot press, using a process that has been previously described.[1] In these experiments bovine leather ( mixed tanned and chrome tanned ) and sheepskin ( glutaraldehyde tanned ) were used as starting materials.

REAGENTS. Urea, tris(hydroxymethyl)aminomethane hydrochloride (TRIS-HCl), sodium dodecyl sulfate (SDS), ß-mercaptoethanol and dimethylsulfoxide were from Merck (grade *pro analysi* ) and used without any further purification. Aqueous solutions were made with deionized/double distilled water (resistivity greater than $4 \times 10^6$ ohm cm).

SOLUBILITY MEASUREMENTS. The samples of natural and processed leather were ground in a blender or in a mortar, washed with ethanol and dried overnight at 60 °C. The resulting powder (20 mg) was taken up in 2.0 $cm^3$ of the chosen solvent and placed in an ultrasonic bath for 17 hours. After centrifugation (at 10,000 rpm for 15 minutes) the supernatant was removed. The remaining solid was then suspended in deionized water (1.5 $cm^3$), centrifuged for 5 minutes and the supernatant removed. This process was repeated with ethanol, and the remaining solid was then dried by lyophilization and weighted. The solubility was calculated as the ratio of weight loss to initial weight.

## RESULTS

SOLUBILITY TESTS. Amino acid composition of the leather samples before and after processing were very similar (Table 1), thus indicating that no significant amino acid degradation took place.

Extensive solubility tests were performed with alcohols, ketones and saturated and unsaturated hydrocarbons. In all these organic solvents ground and processed leather were almost insoluble. Ground leather is slightly soluble in dimethylsulfoxide and the solubility of processed leather is higher, although dependent on the processing variables (temperature, pressure and time). A buffer commonly used for solubilization of proteins of high molecular mass was tried. This buffer consisted of 4M urea, 20 mM tris-HCl , 2% SDS, 0.28% ß-mercaptoethanol, pH 7.2, and the solubilities in this solvent are slightly higher than in dimethylsulfoxide. The relation between the solubility in dimethylsulfoxide and the solubility in the sample buffer is shown on Figure1, and is approximately linear.

SOLUBILITY DEPENDENCE ON PROCESSING CONDITIONS. The samples were grouped in four different sets, named A through D, according to the original tanning process; in all sets the index 0 refers to ground unprocessed leather. The solubility of the different samples and the processing conditions used are reported in Table 2. In Figure 2 the solubility of *pleather* is represented as a function of processing temperature for several samples; each set of points represents identical conditions for the other operational variables : pressure and time. In Figure 3, the solubility is represented as a function of the

processing pressure. For fixed temperature and time, in both figures the solubility of the original ground leather is also represented for comparison.

Series A. In this series ( samples A1-A11 ) mixed tanned bovine leather was used as raw material for *pleather* and it can be clearly seen that an increase in the processing temperature raises the solubility of *pleather* ( Figure 2 ).

Samples A1-A5 ( curve $\alpha_1$ ) were obtained using original leather that was processed for 8 minutes at 600 atm, whereas samples A6-A7 ( 50 atm ) and A8 ( 100 atm ) were processed at lower pressure ( curve $\alpha_2$ ). For samples A9-A10 ( curve $\alpha_3$ ) the starting material was dried prior to be processed. In both sets is , and that predrying the starting material decreases its solubility, as can be inferred by comparing samples A4 with A6 or A5 with A7.

The effect of pressure is not so important as can be gathered by analyzing the solubility of samples A6-A7, but nevertheless the solubility is higher for the greater pressure ( Figure 2 ).

It can also be observed that predried samples treated at temperature below the critical temperature ( ≈ 150 °C ) show much smaller solubilities, but for higher temperatures their solubilities show a marked increase.

Series B. The raw material used in this series ( samples B1-B6 ) was bovine chromium tanned leather that was processed at 760 atm for 8 minutes. The initial solubility of the ground leather must be attributed to the absence of vegetable tanning agents and to a higher degree of inter-fiber binding; again, it can be observed an increase in solubility with temperature is observed ( Figure 2; curve β ) and the existence of a "critical" processing temperature ( ≈ 160 ° C ) can be inferred.

Series C. In this series ( samples C1-C3 ) the batch of bovine chromium tanned leather was the same used in series B, but, prior to processing, chromium was removed with organic chelating agents. The solubilities of the samples thus obtained( Table 2 ) are greater than those of *pleather* obtained from the original leather processed under the same conditions and the results at different pressures also lend support to the assertion that processing pressure is not key factor on the characteristic of the processed material.

Series D. *Pleather* samples in this series ( D1-D9 ) were processed from sheepskin glutaraldehyde tanned leather at 50 and 600 atm for 6 minutes ( except for sample A9, 12 minutes ) at several temperatures. The most striking result is the apparent insensitivity of these samples of *pleather* on the processing conditions ( Figure 2, curve δ ). Sample D10 was processed at 160 °C and 3000 atm for 6 minutes and even under these conditions the solubility is identical to that of the original leather.

DISCUSSION. The solubility data and the amino acid analysis shows that the transformation *leather* → *pleather* for bovine leather is accompanied by a massive destruction of the collagen network without amino acid pyrolysis. The latter view is confirmed by SEM microstructure determination that reveal the destruction of leather fibers and the formation of a continuous material.

From the analysis of the solubility dependence with processing conditions and assuming the solubility correlates well with the transformations induced in leather properties, it can be seen that there is a critical value of processing temperature for extensive transformation of the properties of leather to occur and that this temperature is highly dependent on its origin and on the tanning process used. The influence of pressure is much less marked and above 200 atm, the solubility is almost independent of the processing pressure.

Furthermore, predrying bovine leather raises the temperature of transformation, thus suggesting water must play an important role in the mechanism for collagen cleavage, and that its transformation to *pleather* must take place at higher temperatures.

For sheepskin glutaraldehyde tanned leather the solubility data do not imply such a disruption on the collagen network. A possible explanation for this observation may lie on the small weave angle of the collagen fiber bundles in sheepskin leather thus implying the crossing of the fibers at 'knots' is not so frequent as in bovine hides and so the breakdown of the primitive fibers does not have to take place at the 'knots' as postulated for *pleather* made from bovine leather, and the resulting fibers in *pletaher* from sheepskin are then longer and insoluble in the solvents used. ~~It seems that sheepskin glutaraldehyde tanned leather will not be a good starting material to develop fibre composite materials with good mechanical properties.~~

TABLE 1- Amino acid composition of the leather and some Pleather samples

| Total Amino acids | g/100g | | |
|---|---|---|---|
| | Leather | Pleather II | Pleather IV |
| Aspartic Acid | 1.934 | 2.863 | 2.717 |
| Threonine | 0.856 | 0.87 | 0.833 |
| Serine | 1.523 | 1.634 | 1.531 |
| Glutamic Acid | 4.707 | 4.92 | 4.512 |
| Proline | 4.874 | 4.978 | 4.751 |
| Glycine | 10.586 | 11.096 | 10.727 |
| Alanine | 4.15 | 4.337 | 4.191 |
| Cystine | | | |
| Valine | 1.328 | 1.453 | 1.243 |
| Methionine | 0.288 | 0.356 | 0.323 |
| Isoleucine | 0.707 | 0.661 | 0.66 |
| Leucine | 1.452 | 1.37 | 1.339 |
| Tyrosine | 0.283 | 0.297 | 0.302 |
| Phenylalanine | 0.874 | 1.03 | 0.991 |
| Histidine | 0.354 | 0.357 | 0.333 |
| Lysine | 1.677 | .618 | 1.549 |
| Arginine | 3.32 | 3.49 | 3.481 |
| Amonia | 0.445 | 0.506 | 0.465 |

**TABLE 2.** Solubility as a function of processing temperature and pressure for mixed tanned leather and Pleather of series A, B, C and D

| Sample | P/atm | T/°C | t/min | %S1 | %S2 |
|---|---|---|---|---|---|
| A0 | — | — | — | 46 | 54 |
| A1 | 600 | 76 | 5 | 49 | 48 |
| A2 | 600 | 85 | 7 | 55 | 54 |
| A3 | 600 | 105 | 8 | 59 | 57 |
| A4 | 600 | 120 | 6 | 69 | 64 |
| A5 | 600 | 150 | 8 | 91 | 81 |
| A6 * | 600 | 120 | 6 | 52 | 57 |
| A7 * | 600 | 155 | 10 | 55 | 53 |
| A8 * | 600 | 162 | 8 | 87 | 83 |
| A9 | 50 | 110 | 9 | 61 | 58 |
| A10 | 50 | 155 | 9 | 80 | 79 |
| A11 | 100 | 105 | 8 | 62 | 61 |
| B0 | — | — | — | | |
| B 1 | 760 | 130 | 7 | 23 | 18 |
| B 2 | 760 | 140 | 7 | 19 | 14 |
| B 3 | 760 | 150 | 7 | 23 | 13 |
| B 4 | 760 | 160 | 7 | 29 | 16 |
| B 5 | 760 | 170 | 7 | 41 | 20 |
| B 6 | 760 | 180 | 7 | 81 | 81 |
| C 0 | — | — | — | 43 | 39 |
| C 1 | 200 | 160 | 7 | 88 | 84 |
| C 2 | 750 | 160 | 7 | 97 | 92 |
| D0 | — | — | — | 20 | 18 |
| D1 | 50 | 110 | 6 | 23 | 17 |
| D2 | 50 | 120 | 6 | 21 | 17 |
| D3 | 50 | 130 | 6 | 23 | 17 |
| D4 | 50 | 155 | 6 | 22 | 18 |
| D5 | 600 | 110 | 6 | 21 | 19 |
| D6 | 600 | 120 | 6 | 23 | 17 |
| D7 | 600 | 130 | 6 | 22 | 17 |
| D8 | 600 | 155 | 6 | 21 | 18 |
| D9 | 600 | 155 | 12 | 23 | 18 |
| D10 | 3000 | 160 | 6 | 24 | 16 |

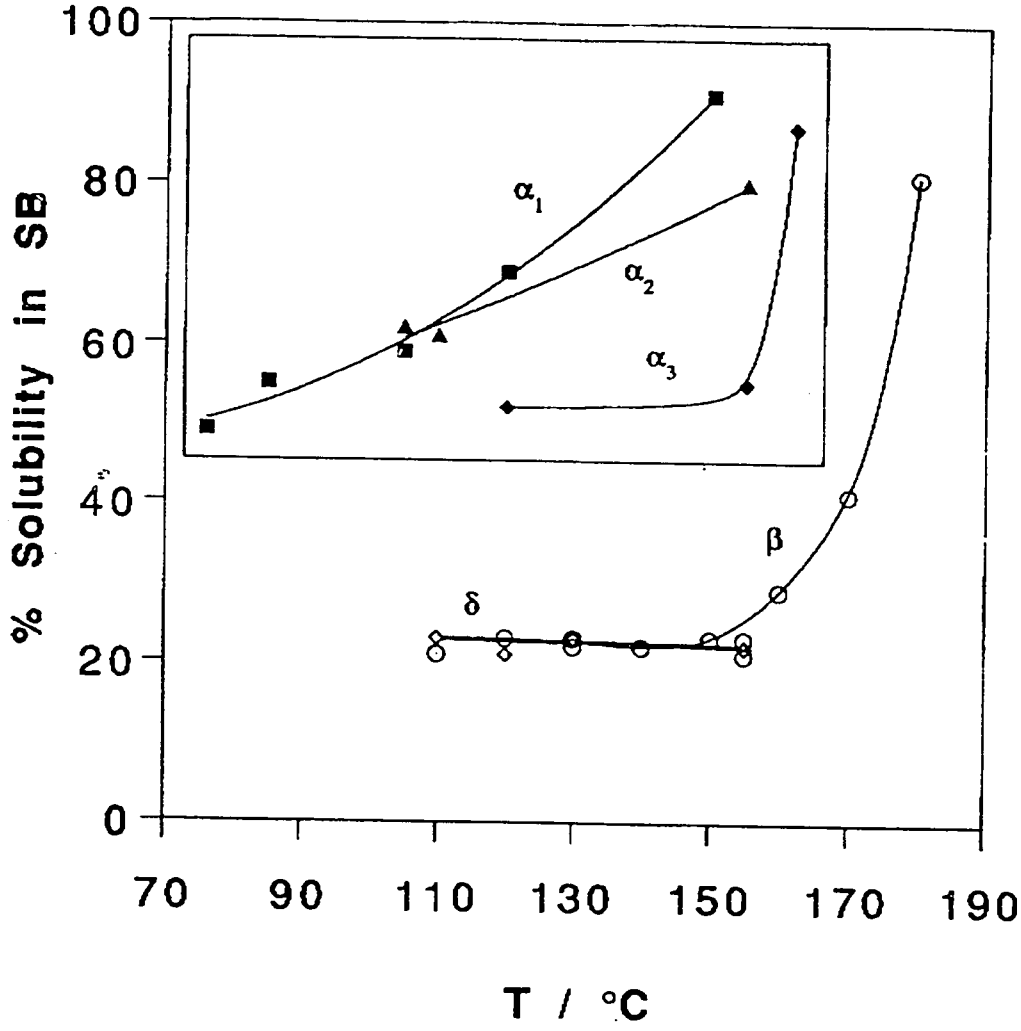
100
80
60
40
20
0
% Solubility in SB
70
90
110
130
150
170
190
T / °C
α1
α2
α3
β
δ

FIG.