Evaluation of operating and mixing conditions of a polymer dispersion co-vinyl acetate and ester acrylic to obtain recovered leather

Evaluación de las condiciones de mezclado de una dispersión co-polimérica de vinil acetato y éster acrilico con residuos solidos de cuero

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Resumen— El trabajo presenta el desarrollo de un diseño experimental que permitió evaluar las condiciones de operación del proceso de obtención de láminas de cuero recuperado con aglomerante. Para llevarlo a cabo se hicieron pruebas preliminares de obtención del material, para seleccionar las variables del proceso que más afectaban las condiciones finales de la lámina de cuero recuperado. Seguidamente, se realizó un diseño de experimentos tipo 2^k, en donde k=4 variables, correspondiendo a: porcentaje en peso de agua, relación másica de aglomerante / cuero, presión y temperatura de curado. Se procedió a la obtención del material y su posterior caracterización, midiendo resistencia a la tensión, porcentaje de compresibilidad, resistencia al desgarre y porcentaje de absorción de agua. Como resultado se obtuvo que los factores principales que optimizan, las variables de respuesta en los niveles estudiados son: la temperatura de curado en el nivel bajo y la cantidad de aglomerante en el nivel alto, mientras que para el porcentaje de absorción de agua también fue significativo la cantidad de agua agregada durante el proceso. Se compararon las características del material obtenido, con las de las plantillas para zapatos y se obtuvieron resultados superiores de resistencia al desgarre, porcentaje de compresibilidad y porcentaje de absorción de agua. Por último se concluyó que a través de la implementación del proceso de reciclaje de cuero sugerido en el trabajo, se obtuvieron láminas de cuero recuperado, cuyas propiedades permitirían tener aplicación industrial.

Palabras clave— cuero recuperado, desechos sólidos, caracterización de materiales.

Abstract— This paper presents the development of an experimental design that evaluated the operating conditions of the process to obtain binded recovered leather sheets. Preliminary tests were performed to obtain the material, and to select the process variables that affected the most the bonded leather sheet final properties. Then, an experimental design type 2^k was run, where k = 4 variables corresponding to the percentage by weight of water mass ratio of binder leather, pressure, and curing temperature. The obtained material was characterized by tensile test, percentage compressibility, tear strength, and water absorption percentage. The result showed that the main factors that optimize the response variables in the levels studied were: the curing temperature in the low value and the amount of binder in the high level, whereas for the water absorption rate was also significant amount of water added during the process. The properties of the material obtained were compared to commercial shoe insoles and the results were superior on: tear resistance, compressibility and percentage rate of water absorption. Finally, it was concluded that through the implementation of the recycling process suggested, recovered leather sheets properties would allow industrial application.

Keywords— Solid waste, recovered leather, materials characterization.

I. INTRODUCTION

The tanning process consists on transformfing animal skin in leather, being mineral-tanning the most efficient in reducing processing time [1]. In each of the leather tanning phases is generated an appreciable amount of solid waste that usually ends up in landfills. Currently the landfill in

Bucaramanga takes in approximately 800 Tn of garbage per day, of which 2% comes from leather waste resulting in about 480 tons per month [2].

In 2010, the Colombian leather industry had growth in production and total sales for shoes of 14.2% and 16.3% respectively over 2009. In 2010, according to DANE, leather goods experienced a growth of 17.4% in production and 13.2% in sales, while exports and imports registered growth of 22% and 26%. The leather manufacturing industry experienced growth in 2010 compared to 2009, production and sales, with 10.5% and 10.7%, respectively. On the other hand, leather imports in 2010 amounted to 7% over the previous year [3].

It is shown then that the volume of leather thrown into Carrasco landfill is considerable and according to production projection, said volume will increase. This paper presents an alternative for obtaining a fibrous material from leather solid waste which could be used by the leather goods industry.

II. LITERATURE REVIEW

Different studies have been carried out seeking the development, with different purposes, of leather solid waste. FRIEDMAN [4] patented a rather simple method that worked by superposing small glued leather disks onto another until forming a solid cilinder which could be sliced to form leather strips. Woodruff [5] filed for a patent for the manufacture of artificial leather through "the use of fibrous material in an aqueous rubber dispersions of the nature of latex as raw materials". BEVAN [6] patented a method of forming a leaher sheet from leather fibers consisting of a series of steps in which is a tangle of fibers is exposed to a liquid high pressure jets on its surface which causes the fibers to be even more entangled forming, then a fibrous surface. However, the latter three authors did not report any performance values. YANIK et al [7] studied the performance of leather waste pyrolysis obtainning carbon residues, which were used for activated carbon. Kindlein et al. [8] obtained leather sheets from bound layers of leather scrap using hot melt techniques. Moreover, DIMITER [9] patented a process that pulverized and mixed leather fiber with a molten resin of vinyl ethyl acetate, in a ratio of 25% by weight, obtainning recovered leather sheets with high impact resistance, electrical stability and permeability. HENKE [10] mixed leather fibers with a binder dissolved in a solvent, using a reinforced mesh between fibers and a polyvinyl chloride paste obtaining a recycled extruded leather sheet with flexibility and tensile strength similar to those of real leather. DA FONTE et al [11] crushed waste leather and aminoplast resins mixed with a proportion of 30 to 40% by weight using catalysts and carrying out curing over a hot press. ADDIE and FALLS [12] obtained recycled leather sheets following the methodology by DA FONTE using, during mixing, 20% by weight of binder and adding water to the process without the use of catalysts.

The most common binders used to bind leather and textile fibers are designed based on acrylic monomers [13], which can be polymerized with other organic and inorganic ingredients to form a latex film which gives properties such as adhesion and stability to the fibers mixed with said binder.

Other types of adhesives, such as PVC used for laminated panels [14] are based on urea and formaldehyde whose application was introduced in 1937 as an adhesive paper [15]. For this case-study, it was used a binder of vinyl acetate and acrylic ester, because the acrylic adhesives are soluble in water [13] and the monomers vinyl acetate have low flaming points, which facilitate handling, being the premium main material for adhesives [14].

It is shown that the intention of reusing waste from tanning and leather prodcution are not isolated even for products other than those proposed in this case.

Methodology

To determine the operating conditions of mixing and pressing leather solid waste with a binder from an experimental design, preliminary tests were performed to select the design variables. Then a 2^k type experimental design was performed [17], where k=4 variables corresponding to: percentage by weight of water, mass ratio of binder / leather (during mixing), pressure, and curing temperature (during pressing). Two levels were taken for the design variables: high and low. The result of said design yielded 16 scenarios. Then the material was obtainned according to the design and subsequent characterization by measuring stress, percentage of compressibility, tear

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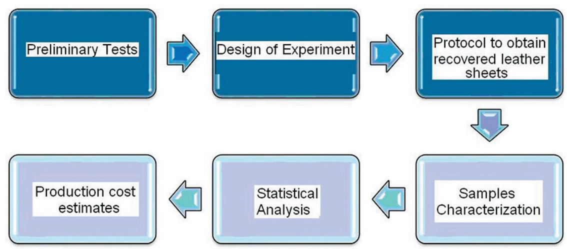
and percentage of water absorption. Additionally, it was conducted a preliminary economic analysis of cost per unit area of recycled leather. Figure 1 shows the methodology for this study.

Fig. 1. METHODOLOGY STEPS



There were carried out the 16 scenarios and a replica of each. Particles were ground to a size of 2 mm, then they were mixed with water and binder and were cured for 15 minutes. Table I shows the high and low values for the used variables. To select these values, it was taken into account values reported in the literature review. Preliminary tests showed results that allowed selection of the levels for the design of the experiment.

TABLE I

RANGES OF PROCESS VARIABLES USED

Variable	**High level (+1)**	**Low level (-1)**
Pressure	150 Kg f/cm²	100 Kg f/cm²
Temperature	80 °C	70 °C
% binder /leather	3/7	2/8
% by weight of water	25	15

To characterize the obtained samples, a Shimadzu ® universal testing machine was used. The machine was equipped with a load cell of 1 kN for tensile tests and for the compression test it was equipped with a 100 kN cell. The tests were done according to standards ASTM D1610-01, D6015-10, D2209-00, ASTM D2212 and ASTM D2213. Table II shows the geometric notation design of experiments.

Data statistical analysis was performed using STATGRAPHICS CENTURION 16.

TABLE II

GEOMETRIC NOTATION

Scenario	P	T	% binder / leather	% by weight of water
1	-1	-1	-1	-1
2	+1	-1	-1	-1
3	-1	+1	-1	-1
4	+1	+1	-1	-1
5	-1	-1	+1	-1
6	+1	-1	+1	-1
7	-1	+1	+1	-1
8	+1	+1	+1	-1
9	-1	-1	-1	+1
10	+1	-1	-1	+1
11	-1	+1	-1	+1
12	+1	+1	-1	+1
13	-1	-1	+1	+1
14	+1	-1	+1	+1
15	-1	+1	+1	+1
16	+1	+1	+1	+1

Results

In Figures 2, 3, 4, and 5 the circles represent experimental data, the diamonds represent data from the replicas and triangles represent data from verification tests 2, 5 and 9, according to the values shown in Table 2. The dotted line in Figures 2, 3, 4 and 5 corresponds to the average values of each of the tests performed on the material used in the preparation of insoles.

Figure 2 shows that the third test showed the highest tensile strength value with 5.57 MPa and a low percentage of error between duplicates.

Fig 2. TENSILE TESTS RESULTS

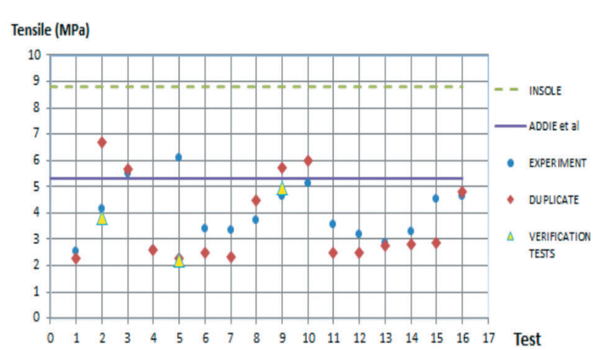


Figure 3 shows that the maximum tear resistance was exhibited by samples 2, 9 and 10, with a value of 694 N exhibited by sample number 10.

Fig. 3. SLIT TEAR RESISTANCE TEST RESULTS

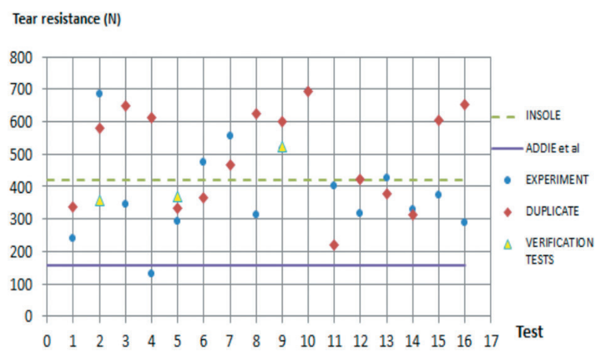


Figure 4 shows that the percentage of compressibility obtained for the samples was about 10%, which is below 18.5% obtained for commercial insoles.

Fig. 4. PERCENTAGE OF COMPRESSIBILITY RESULTS

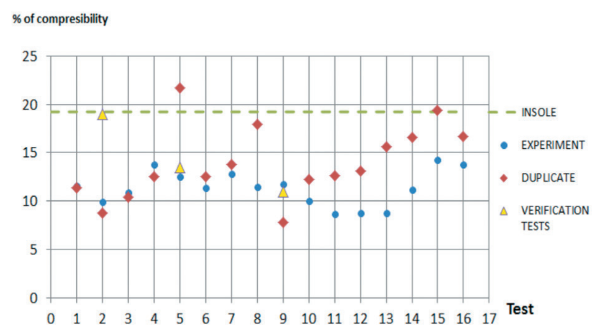
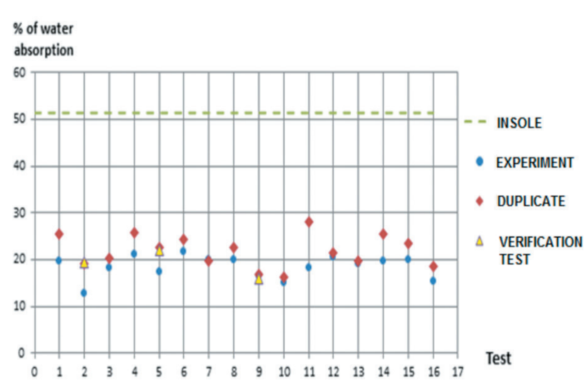


Figure 5 shows that the tests 9 and 10 report the lowest percentage of water absorption with a 16 and 17% respectively and with the least error between duplicates. When compared with the reported value of the material used in the manufacture of insoles, it was observed that lower values were obtained.

Fig. 5. PERCENTAGE OF WATER ABSORPTION RESULTS



Discussion

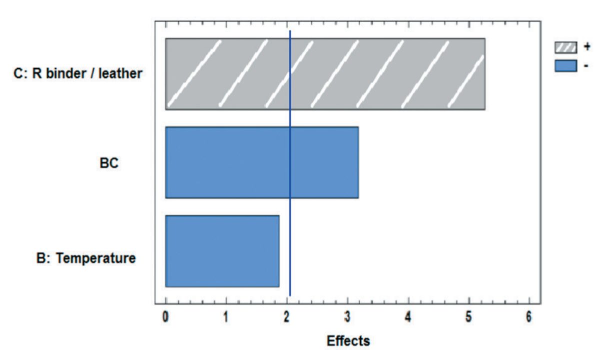
In figure 2 is shown, as a solid line, the average results of tensile strength reported by ADDIE AND FALLS [12]. Said values are above for those obtained in this work. However, when comparing the values of tear resistance, Figure 3 shows that values were higher than those reported by the same authors.

SILVA [19] after characterizing 86 samples of safety footwear leather, obtained an average tensile strength quite high compared with those obtained in this work, but he also reported tear resistance values consistent with those reported in figure 3.

Concerning the percentage of water absorption is desirable it is minimal. According to [17], citing 2396 NTC, insoles footwear must meet a percentage of maximum water absorption of 50 ± 2%. The values shown in Figure 4 show that it meets said standard.

A Pareto analysis shows the effect of process variables and their influence on it. For example, in the Pareto diagram of Figure 6, it is appreciated the amount of binder added to the process is significant on the samples tensile strength, The best combination is obtained by keeping pressure, temperature and water amount at a low level and the relationship binder / leather at a high level.

Fig. 6. PARETO ANALYSIS FOR TENSILE STRENGHT



It is seen in the Pareto chart in Figure 7 how tear strength depends significantly on the relationship binder / leather. This allows assessing the best mixing arrangement for maintaining the same conditions reported for maximum tensile strength under levels studied.

Fig. 7. PARETO ANALYSIS FOR TEAR STRENGHT

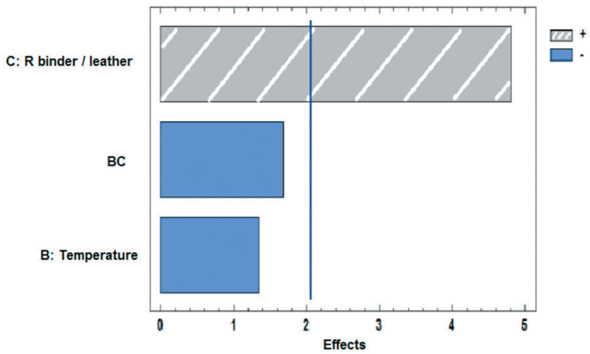
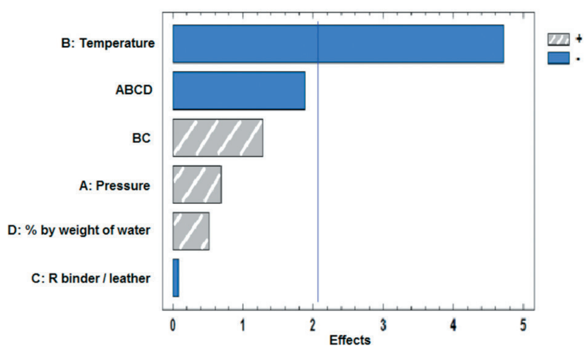


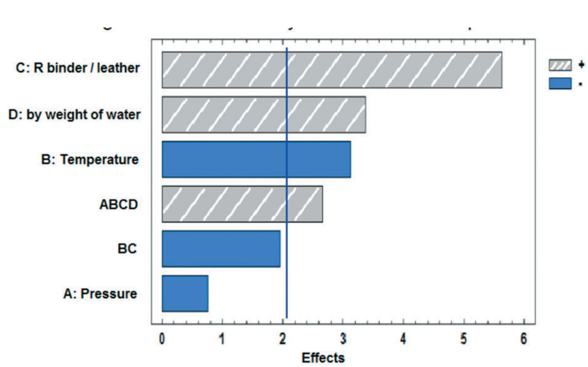
Figure 8 shows the Pareto analysis for the percentage of compressibility test, being temperature the main cause of the variation. For the percentage of compressibility, the best arragment corresponds when the four variables are in low level because it requires the least material deformation.

Fig. 8. PARETO ANALYSIS FOR PERCENTAGE OF COMPRESSIBILITY



Pareto diagram in Figure 9 shows the variables that cause effect on the percentage of water absorption. It is appreciated that this depends on the pressure and temperature in their low level and the amount of binder and water in their high one.

Fig. 9. PARETO ANALYSIS FOR WATER ABSORPTION



The summary of the best combinations found are shown in Table III

TABLE III
OPTIMAL VALUES OF VARIABLES USED

Variable	Pressure (Kg / cm2)	Temp (°C)	% binder / leather	% by weight of water
Tensile	100	70	3 / 7	15
Tear Strenght	100	70	3 / 7	15
% Compressibility	100	70	2 / 8	15
% water absorption	100	70	3 / 7	25

Finally, a preliminary estimate of costs for recovered leather sheets was made for production of 1 Tons per day. This was done in order to assess the process economic viability. There were considered initial invesment cost, direct costs of manufacturing and fixed manufacturing costs [16] for the first year of production.

For initial investment were estimated only equipment, whereas for manufacturing direct costs were included raw materials, industrial services, supplies, labor, maintenance and repair. For fixed manufacturing costs were considered the depreciation of equipment, insurance and taxes. Table IV shows the estimated costs in Colombian Pesos.

TABLE 4
TOTAL COSTS FOR THE FIRST YEAR IN PRODUCTION

Total cost of production (thousands $)	
Initial invesment	53.000
Manufacturing direct costs	1.079.350
Fixed manufacturing costs	6.996
Total ($)	1.139.346

Dividing the total cost by the annual production, it yields a value of $10,100 per sheet of 1.5 m^2. When compared to the cost of an insole sheet, which oscilates around $ 7,000 for the same dimensions, it is evident that the proposed process for recycling leather is not viable economically, but it is technically and environmentally. However, comparing with the cost of recovered leather sheet placed in Bucaramanga, which has a cost of $ 48,000 per 1.5 m^2 [18], the process turns out economically viable. Additionally, there will be a reduction in costs, not quantified in this study, associated with the reduction of space in landfills, waste transportation and disposal.

CONCLUSIONS

The temperature and relation binder / leather bear a significant influence over response variables, during pressing and mixed respectively.

The most significant factor on the four 4 response variables, based on the levels studied during the pressing stage, corresponds to the curing temperature in the low level (70° C).

The values obtained for the percentage of compressibility and percentage of water absorption are low compared with values obtained for commercial insoles. This gives flexibility to manipulate the weight percentage of water during mixing. That is, if one wants to choose a combination where one gets the best response variables within the studied levels, it becomes a cost / benefit where the amount of water, although it was raised at a low level for tensile strength, tear and percentage of compressibility, can work at a high level, because the increase in process water reduces the mixing time. This should be reflected in the reduction of the mixer power consumption.

The pressure should be maintained at low level, the temperature in the low level and the relationship binder / leather in the high level, since this appears to produce no significant effect on the percentage of compressibility.

It was thought initially that recovered leather sheets would exceed tear strength, percentage of compressibility and the percentage of water absorption, compared with the same properties of commercial insoles. However, if the final product does not require reaching values of tensile strength, the material obtained with the proposed method has the ability to replace it.

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