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## WASTE LEATHER PARTICLES AS A FILLER FOR POLY(VINYL CHLORIDE) PLASTISOLS

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Key Words: Plastisol, Poly(vinyl chloride), Waste Leather, Filler, Surface Treatment, Recycling

### ABSTRACT

Waste leather granules were incorporated into poly(vinyl chloride) plastisols containing di-octyl phthalate as plasticizer. The rheological behavior and gelling characteristics of plastisols were investigated and the filled samples were tested for their physico-mechanical properties. It was found that density, wear resistance and Shore D hardness of composites increase whereas the tensile properties are considerably deteriorated with the incorporation of leather. In order to improve mechanical properties, treatment of the leather granules was applied with a solution of ethylene vinyl acetate (EVA) copolymer. This seemed to produce a coating that promotes adhesion as well as proper wetting of the granules and, thus, significantly improves the tensile characteristics of specimens. The upper level of leather content, in order to produce filled products with acceptable properties, was estimated at the concentration of 50 phr. This is an extension to the limits of the system plasticized poly(vinyl chloride)/leather determined in the case of its processing via melt mixing techniques.

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## INTRODUCTION

It is well known that waste management has become a major problem in modern societies. The concern of environmentalist groups has often focused on solid waste with potential toxic effects, thus creating restricting legislation. The authorities have formulated plans in order to face pollution problems on a safe basis, allowing at the same time enough space for industry to work. The European Community has based its waste management strategy fundamental principles, such as prevention and reduction of waste, and increase in the recycling and safe disposal of unavoidable waste [1]. Therefore, it is important that products make the least possible contribution, by their manufacture, use or disposal, to increase volume or harmfulness of waste and aggravating pollution hazards [2].

Leather scraps after chromium tanning represent a widely recognized source of waste. In fact, in 1996 approximately 45% of footwear made worldwide was leather, which equates to 4.150 million pair of shoes. To make these goods, an estimated 6.750 million ft<sup>2</sup> of leather was processed. Assuming an average of 30% scrap, this gives 2.025 million ft<sup>2</sup> of waste leather in 1996 [3]. In addition, these sources of scrap can have potential contribution to environmental pollution, taking into account that chromium treated products are classified in the first category of hazardous waste. About 90% of the total waste leather is chromium tanned and, more specifically, consists of:

Leather scraps containing up to 12.5% nitrogen, 2% fat, 3.5-5% Chromium (III) and a minimum of 30% moisture

Tanning solid wastes, deriving after trimming and splitting, with the same as above composition with the exception of higher water content (up to 70%).

Various processes have been proposed for the hydrolysis of leather waste and preparation of fertilizers, specified for different agricultural applications [4]. Furthermore, studies for the development of recycling processes for waste leather fibers have been conducted, focusing on composite materials containing a polymeric matrix and the leather fibers as a filler at various concentrations [5].

In a previous work [6], an attempt was made to prepare and study some blends based on polymeric matrices containing the leather particles as a dispersed phase. These composites were expected to combine properties that allow their use in the shoe industry, as a substitute of the pure raw materials. Among various polymeric matrices, including thermoplastics and rubbers, plasticized poly(vinyl chloride) (PVC) was found the most promising material due to its low cost and versatility.

Regarding rheological properties of the PVC compounds, studied in a torque rheometer, it was clear that a linear increase of torque with leather content up to 40 phr takes place, due to the increase of melt viscosity at higher filler concentrations. Similar results have been published by Santana and Marquez [7] who studied the incorporation of leather fibers in PVC containing 45% plasticizer. The above researchers also employed a Brabender plasticorder, working at 180°C and 10-50 rpm roller speed, and found that an about linear increase of the torque is established for leather concentrations up to 40%. On the other hand, Santana and Marquez reported a decrease in torque for higher leather concentrations, whereas in our work the incorporation of filler beyond this point appeared to cause a sharp increase of the viscosity of PVC melt and consequently, of the mixing torque. It should be noted that, increasing the mixer temperature, which certainly would lower the melt viscosity, should be a potential hazard for degradation of the over-heated polymer due to its poor thermal stability.

Therefore, it seemed interesting to explore the possibilities of using PVC plastisols instead of the plasticized matrices that require melt mixing technique for further processing. This procedure enables us to avoid exposure of the polymer at high temperatures for a long time. In addition, plastisols offer the advantage of low initial viscosity that allows better wetting of the leather granules and guarantees improved interfacial properties of the final specimens.

## EXPERIMENTAL

### Materials

Emulsion grade polyvinyl chloride (Etinox-430, supplied by Aiscondel S.A. Spain) was used for making plastisols.

The resin Etinox has the following characteristics:

<b>K Value</b>	<b>Specific Viscosity*</b>	<b>Particle size distribution less than 0.063 mm (%)</b>	<b>Volatiles (max.) (%)</b>
72	0.506	99.9	0.3

\*The specific viscosity is measured at 25°C, using a solution of 0.4 gr of resin in 100 ml of cyclohexanone.

DOP was the plasticizer used at the concentration of 80 phr. Also, 2.5 parts of a Cadmium/Zinc (Cd/Zn) heat stabilizer per 100 parts of PVC were

added in order to prevent the blend from heat degradation during gelation and molding.

Finished leather granules with an average particle size of 1.5 mm were used as the filler. These granules were produced after grinding and sieving the finished scraps.

A copolymer of ethylene and vinyl acetate (EVA) containing 25% vinyl units (Cryovac S.p.A., Italy) was used for surface treatment of leather granules, before their incorporation into the polymeric matrix. EVA was dissolved in boiling toluene (technical grade) at concentrations of 2.5% w/v and the solution was poured in leather particles so that the dry leather contains 2% w/w EVA. It was found that the minimum volume for complete wetting of 100 g of leather particles is 80 ml solution. The wet leather particles were then dried at 100°C for 1 hour, in an air oven.

### **Preparation, Characterization, and Molding of Plastisol**

The plastisol compounds were prepared by simple mixing of the components, (i. e., suspension grade PVC: 100 parts, DOP plasticizer: 80 parts, heat stabilizer Cd/Zn: 2.5 parts) using a motor driven stirrer.

The variation of viscosity of the prepared plastisols was followed by the use of a Brookfield viscometer (Brookfield Synchro-Electric, MA) equipped with a spindle no 6, of the RVT series. This instrument is capable of displaying the torque on a rotating spindle into the viscous plastisol, in arbitrary units. The data obtained can be transformed into viscosity by using the suitable tables. As was expected, rheological behavior of plastisols is far from that of newtonian fluids and therefore, the rotation speed of the spindle was adjusted to 10 rev/min and 20 rev/min in order to compare the values corresponding to different shear rates. Furthermore, measurements were obtained after 3 minutes of agitation, since some dependence of the viscosity on the shearing time would be expected.

The same as the above type of viscometer, equipped with a heating mantle, was also employed for the determination of gelation characteristics. The temperature rise was adjusted at 1°C/min and continuous measurements of the viscosity were run. Under these measurement conditions, gelation temperature was considered the point of the sharp increase of the viscosity.

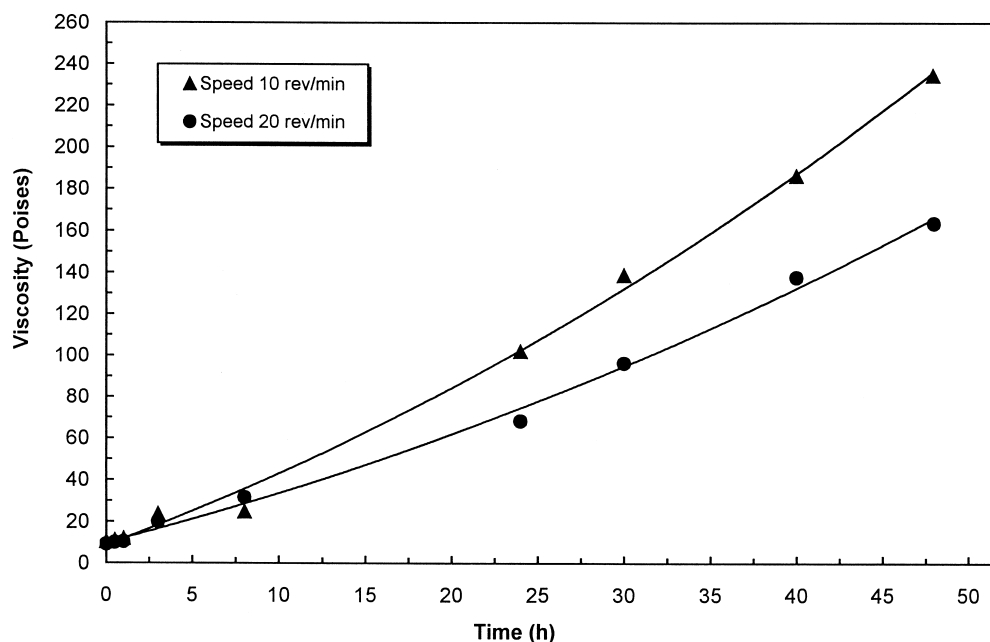
Two types of leather granules, i.e., the materials, as received and surface treated with EVA solution, were added at various concentrations and dispersed into the plastisol. The mixtures were then placed between two steel plates and heated at a temperature of 150°C for 30 minutes. Specimens were cut from the obtained sheets for subsequent testing of their properties.

### Testing of Properties

Mechanical measurements were made according to ASTM D-638 specification. An Instron tensometer 4466, equipped with a load cell of maximum capacity of 5 kN was used, working at grip separation speeds 50 mm/min due to the flexibility of specimens under test. For the density measurements, the ASTM D-1505 specification, using the column gradient technique was followed. For calculation of the density value, the mean of three measurements was used. The hardness measurements were carried out according to a ASTM D-2240 specification, using a Durometer of the scale Shore D. In all cases, the average of ten measurements was calculated. Finally, the wear resistance of filled specimens containing up to 40 phr of leather was determined following the ISO 4649:85 specification, method A.

## RESULTS AND DISCUSSION

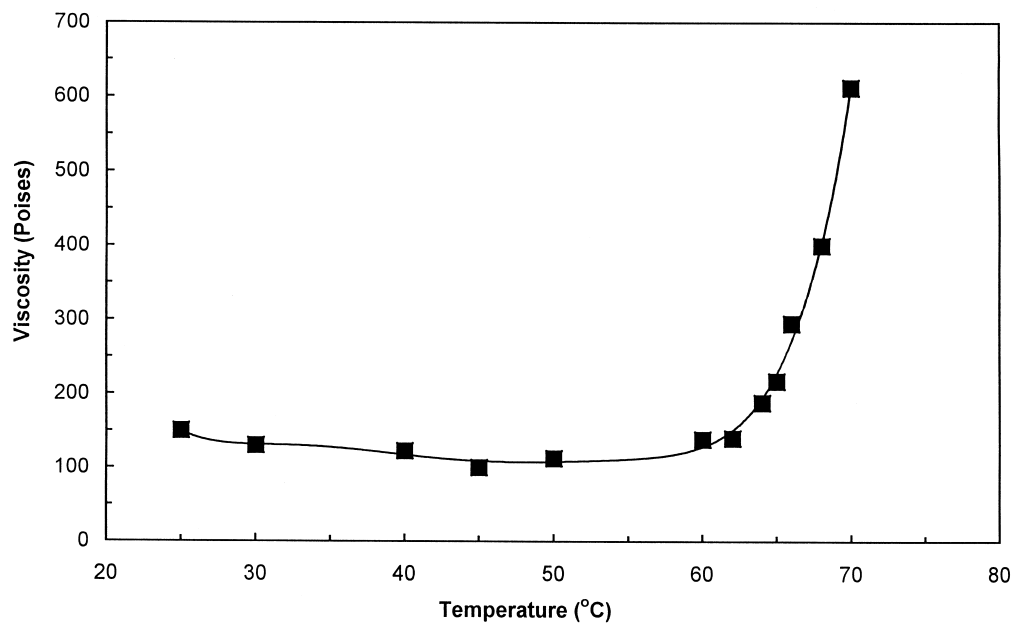
The dependence of viscosity on the aging time is presented in Figure 1. From the curves of this Figure, it is evident that the initially low viscosity of plas-



**Figure 1.** Brookfield viscosity of plastisol vs. time, at 20°C.

tisol shows an increase with time. In fact, as soon as the mixture is prepared by dispersing the emulsion grade PVC particles into the plasticizer at room temperature, a low viscosity slurry is produced that allows free flowing of the PVC particles in the liquid phase of DOP. Upon ageing of the above product at room temperature, solvation, swelling and dissolution of the PVC particles take place and thus, the slurry gradually turns to a viscous dough. Comparing the two curves of Figure 1, it is clear that the plastisol studied in this work, behaves as pseudoplastic fluid throughout the whole period of aging. This can be established by the differences observed in the determined viscosity values for different rotation speeds of the spindle. In fact, lower viscosity corresponds to 20 rev/min which reflects an increased shear rate compared to that imposed by a rotation speed of 10 rev/min. Most interesting, the pseudoplastic character of plastisol increases with time since the two curves deviate more after 48 hours of aging.

Figure 2 presents the viscosity of the prepared plastisol as a function of temperature. It is evident that temperatures up to 50°C tend to reduce viscosity. Then, an abrupt increase is recorded, which suggests that the gelation area of the plastisol under investigation lies within the range 60-70°C, depending on the exposure time. This must be taken into consideration when handling plastisols and avoid their exposure to that high temperatures, in order to prevent them from



**Figure 2.** Brookfield viscosity of plastisol as a function of temperature.

TABLE 1. The Density of Filled PVC with Various Loads of Leather

Filler Conc. phr	Density g/ml
0	1.178
20	1.211
30	1.230
40	1.255
50	1.271

being gelled, which prohibits further processing. On the other hand, the determination of gelling temperature is necessary for the proper design of the moulding procedure.

Some of the physical properties of the systems prepared by loading PVC plastisol with leather granules, are presented in Tables 1 and 2. In fact, the density of the filled polymer, is obviously a function of leather concentration and displays an increase with it. It is very interesting, taking into account the densities of pure plastisol and leather (1.178 g/ml and 1.32 g/ml respectively), that it can be concluded from the data of Table 1, that a volume retraction occurs after mixing the components of this system. This suggests that some interactions between matrix and filler take place, such as reduction of the porosity of leather granules due to better wetting by the low viscosity palstisol. This in turn, could be an evidence of improved interfacial characteristics between the PVC matrix

TABLE 2. The Shore a Hardness of PVC/Leather Blends

Leather Content phr	0	20	30	40	50
	19	25	26	36	41
	17	23	24	30	40
	17	25	23	36	41
	18	25	28	33	33
	21	23	29	34	35
	20	20	26	35	42
	16	26	24	35	38
	16	24	27	32	37
	18	26	26	29	33
	16	25	26	28	34
Average	17.7	24.2	25.9	32.8	37.4



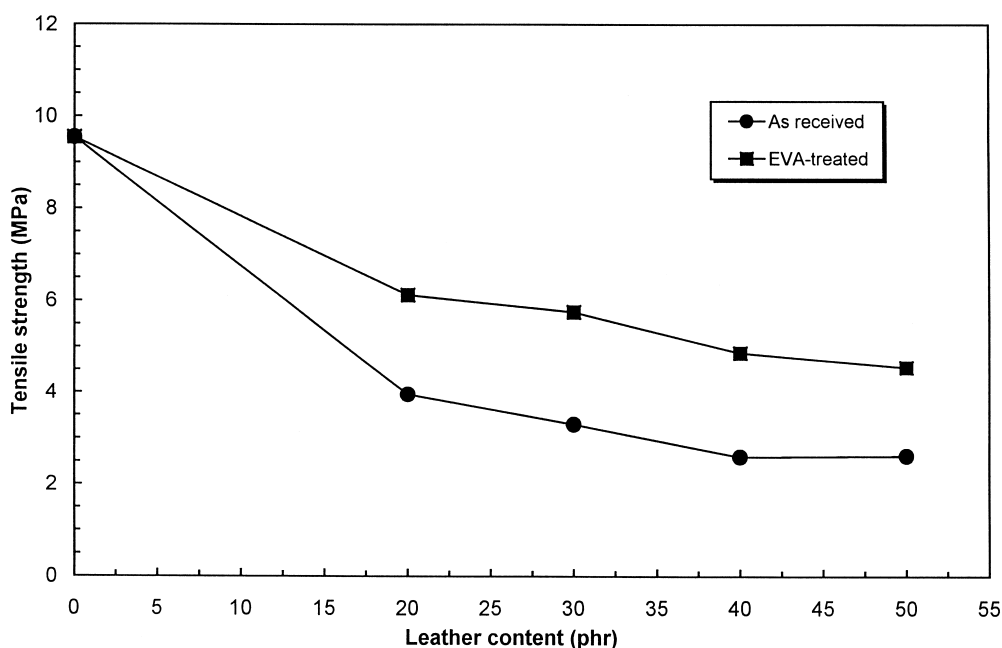
TABLE 3. The Wear Resistance of Filled PVC with Various Loads of Leather

Leather Content phr	Volume Loss mm <sup>3</sup>
0	259.4
20	264.0
30	239.8
40	222.5
50	208.7

and the as received leather granules whose the outer surface contains many voids and macropores.

Similarly, Table 2 shows the Shore hardness of the specimens prepared. An increase of the hardness value is evident, as the content of leather increases. This was an expected fact, since tanned and finished leather has considerably higher hardness than that of the soft, plasticized polymer. This should be of importance when the wear properties of such systems are evaluated. As a matter of fact, the hardness values are a measure of the wear resistance because hard materials resist better in friction and wear. In fact, Table 3 shows the volume loss of specimens containing up to 50 phr leather, tested for their wear resistance. As mentioned before, the wear resistance becomes higher with increasing leather concentration, since those systems display higher values of hardness. However, the pure plastisol shows a lower volume loss than that of filled material containing 20 phr of leather granules. This difference can be attributed to the fact that the soft polymer fills the abrasive paper and therefore further wear during the experiment is inhibited.

The mechanical properties of plastisol filled with both as received and treated leather granules, are presented in Figure 3 in terms of the tensile strength as a function of waste leather concentration. It is evident that significant deterioration of the tensile characteristics takes place upon loading the system with leather particles. Most of the strength decrease occurs for filler concentrations up to 20 phr and then, further changes in strength do not seem significant. Similar results were obtained with PVC/leather blends prepared by melt process [6], but the above mentioned restrictions do not allow us to exceed 40 phr of leather. In the case of palstisols, it would be reasonable to suggest that 50 phr of leather content is a safe limit in order to produce workable materials with acceptable mechanical properties.



**Figure 3.** Tensile strength vs. filler content of filled plastisol.

Further improvement of mechanical behavior of the produced specimens was attempted by incorporating into the plastisol matrix treated leather granules, since pre-treatment of the surface of various fillers before their incorporation into polymeric matrices is a very common practice in plastics processing [8-11], aiming at the optimization of interfacial characteristics between matrix and filler, which is necessary in order to obtain improved final properties. More specifically, could be expected by applying a suitable coupling agent or adhesion promoter [12]. In the case of plastisol-leather systems, coating of the surface of granules with a polymer capable of developing adhesive bonding with plasticized poly (vinyl chloride) seemed to be the recommended selection. Therefore, the treatment consisted of surface coating of the granules with a thin film of ethylene-vinyl acetate copolymer. The results are shown in Figure 3, where the curve corresponding to treated granules reflects an impressive increase of strength. This can be attributed to the enhancement of adhesive bonding between matrix and granules, as explained above. Moreover, moisture is expelled from the EVA treated leather during drying of the toluene solution and, also, the coating reduces macroporosity of the granules, thus making their surface more regular and easier to be wetted by the plastisol.

## CONCLUSION

This work showed that chromium treated, finished waste leather granules could be a potential filler for PVC plastisols leading to final products with easy process and acceptable properties. It was found that the density, wear resistance and Shore D hardness of the filled specimens are improved, whereas their mechanical properties are considerably deteriorated with the incorporation of leather. Treatment of the leather granules with EVA solution seems to produce a coating that promotes adhesion and proper wetting of the granules, thus improving significantly the tensile. The upper level of leather content taking into account the mechanical and processing characteristics, appeared to be the concentration of 50 phr. This is a significant extension compared with the limit determined for melt process which cannot exceed 40 phr [6].

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