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Application of Extracted and Modified Gelatin from the Leather Solid Waste in Commercial Finishing Agents

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ABSTRACT
Raw trimming has the potential to generate value-added product gelatin which produces the biodegradable film with low physical and mechanical properties. The chemical modifications by using the crosslinking agent improved the performance properties of the gelatin. Commercially produced leather finishing binders are mostly non-biodegradable which have an adverse environmental impact with high grain loading. The binders blended with extracted and modified gelatin can reduce the environmental burdens by replacing a part of non-biodegradable materials from leather finishing agent. In this study, the gelatin was undergone thermal hydrolysis in acidic and alkali conditions at 90°C hot water and after modification of gelatin with cross-linkers it was blended with available commercial binders in an optimized ratio and tests carried out to check whether there is any major change to the performance properties of the finished film. Prepared films showed promising results with the gelatin-protein (PG_m) and gelatin-acrylic (AG_m) formulation. This approach has the implication in leather finishing subject to the assessment of physical properties of the finished film.

Keywords: Gelatin, binders, biodegradable film, performance property.

1. INTRODUCTION

The leather is a valuable outcome of the tannery by processing raw hides and skins, which are the by-products of meat and meat product industry [1]. The finishing process is one of the crucial steps in the processing of leather by which the tanning industry transforms leather into end-product [2]. The purpose of finishing is to improve the use properties of the leather in general and to protect it from wetting and soiling, to level out patches and grain faults and to apply an artificial grain layer to split or corrected grain leather etc. The finishing materials used in leather finishing can be classified into two main groups such as the binders that is main film-forming materials and additives that include colorants, penetrators, fillers, lacquers, feel modifiers, plasticizers, and auxiliaries' etc. [3]. There are mainly two types of binders used in leather finishing such as natural and synthetic binders. Among the natural binders protein (casein, albumens), resin (shellac) and among the synthetic binders resin emulsions such as acrylics, butadiene, polyurethane, hybrids and compact are main. All of these binders have high grain loading, high volatile organic content (VOC). But all these types produce the non-biodegradable film with the artificial look. In that case, biodegradable films can replace existing synthetic non-biodegradable products at the lowest cost possible; focusing on improving quality and shelf life, protecting, and maintaining product integrity and enhancing product appearance. This biodegradable film can be prepared simply with low cost by utilizing solid waste generated from tannery during tanning operations [4]. Solid wastes generated in leather industries include skin trimmings, keratin wastes, fleshing wastes, chrome shaving wastes, and buffing wastes. [5]. Protein is the main component of most of these wastes [4]. The recovery of protein from various tannery residues can be done by hydrolysis at 80-130°C in aqueous acid or alkali [6]. Gelatin is a substantially pure protein obtained by the thermal denaturation of the protein [7]. Due to its functional properties, it has been utilized in the production of edible and/or biodegradable films; the practical use of gelatin extracted from leather waste, as a material, may be limited by its relatively poor physical properties whereupon the material may disintegrate upon handling. To improve the product properties, it is often necessary to introduce exogenous crosslinking into the molecular structure of the gelatin. Crosslinking has shown to improve the physical performance of a film/coating [3]. The main target of this study is to blend the chemically modified gelatin with the commercially available binders to produce a low cost, less nonbiodegradable, low grain loading and comparatively eco-friendly film.

2. METHODOLOGY

2.1 Gelatin extraction

Gelatin was prepared by the treatment of acidic and alkali hydrolysis in hot water (90°C) with a slight modification of the referenced [4] process. The wet salted raw trimming offals were properly washed to remove the salt and chopped into a smaller size. The added water was 5 times more than the trimming weight and allowed to swell by sulfuric acid with proper maintenance of pH for 48 hours. The pH of the solution was 2.5 and it was adjusted by different installment of acid addition. After acidic swelling, the trimmings were divided into two parts. At one part, the pH of the solution was maintained 9.4 for alkaline hydrolysis and for acidic hydrolysis the pH of the solution was kept 4.7. Then, each of them was subject to thermal treatment at 90° C for 6 hours with continuous agitation. After thermal treatment, it was slowly brought to the normal room temperature and filtered. Next, the filtrates were shaken well and slowly stirred at room temperature for 40 minutes. Finally, the resultant solutions were centrifuged at 4000 rpm for 25 minutes and gelatin separated. A part of gelation was preserved at 4° C for measuring the gel strength and the rest was kept at normal temperature with an addition of 0.4% bactericide (BUSAN 30L) to prevent putrefaction.

2.2 Chemical Modification

The aldehyde-based crosslinker (LUXOFIX NH8) was used to modify the gelatin. The crosslinker contains 5% solid and added as a percent (10%) of the gelatin solutions. The mixture was left for curing at the room temperature for 2 hours. Here **Photo1** shows the

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centrifugation process and **Photo2** shows the prepared films.

2.3 The blending of modified gelatin with binders
Three binders such as acrylic, polyurethane, and polyamide protein were collected from a local agent of a reputed leather finishing chemical company. Then, all of them were blended with modified gelatin at a ratio of 70:30 (optimized) to prepare a 2gm film in a 55 mm diameter petri dish. Initially, the Petri dishes were cleaned up and castor oil was used as film releasing agent. After that, the properly mixed binders with modified gelatin were poured on the dish. Then the Petri dishes were stored and left out for drying at room temperature with proper ventilation for film formation.

Photo1: Centrifugation

Photo2: prepared films

The simplified study workflow is illustrated below in **Fig.1**

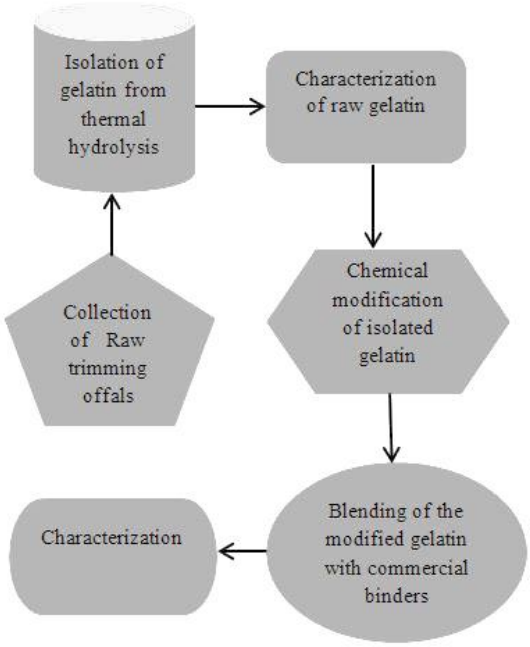

Fig.1 Process flow diagram

2.3 Characterization
Different performance properties of the prepared films with respect to original film such as swelling or crosslinking, rheological property (viscosity at different shear rates), the melting point were analyzed.

2.3.1 Swelling property
Prepared films were analyzed for their water absorption or swelling. The films were weighed and immersed in a physiological solution for different periods of time. Wet samples were blotted with a tissue to remove excess liquid and re-weighed [4].
The amount of absorbed water was calculated as:

$$\text{Swelling } (\%) = 100 \left(W_{wet} - W_{dried} \right) / W_{dried}$$

Where W_{wet} is the weight of the wet sample and W_{dried} is the weight of the dry sample.

2.3.2 Viscosity property
The average viscosities of the samples with respect to different shear rates such as $1s^{-1}$, $10s^{-1}$,$100s^{-1}$ and $500s^{-1}$ were measured. This feature is important for different finishing stages or processes such as can stability, mixing and pumping, and coating application. Each of these processes requires certain viscosity to aid the overall finishing system. Analysis of viscosity helps to build a perspective of applicability of prepared finishing agents.

3.3.3 Thermal analysis
Thermal analysis was carried out by differential scanning calorimeter (DSC) that is a powerful and versatile thermal analyzer allows for property measurements on a broad variety of materials from -150 to 600°C with heat flow range ± 40µw. It is basically a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment.

Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperature to be scanned. The main application of a DSC is in studying phase transitions, such as melting, glass transitions or exothermic decompositions, crystallization time and temperature etc. Samples were stored in a humidity chamber at the prescribed relative humidity (60%) for a minimum of 48 h and 20° C, and the machine needs to stabilize and purging prior to analysis. The dry film (10 mg) was hermetically sealed in an aluminum pan and subjected to a double scan in a differential scanning calorimeter. The scans were carried out at a heating rate of 10° C/minute in the temperature range of 50° to 200° C. All samples were run in triplicate [4]. The result of a DSC experiment is a curve of heat flux versus temperature or versus time. From the curve analysis, the melting temperature of different films can be determined.

3. RESULT AND DISCUSSION

The graphical representation of water uptake (swelling) of 100gm film, average viscosities and thermal analysis of original and modified films are given below. Also, **Table1** shows the characterization property of the original and modified films.

Table 1 Characterization of original and modified films.

Sample	Swell (water per 100 gm film)	Melting point, °C	Average viscosity, mPa.s Share rates			
			1 s^{-1}	10 s^{-1}	100 s^{-1}	500 s^{-1}
A	29	167.11	127	17	30	52
P	2537	118	1129	124	110	224
PU	23	207.48	1104	1049	846	467
G	4000	65.06	11	9	24	34
G_m	193	85.42	112	13	19	36
AG_m	128	126.81	225	39	33	53
PG_m	229	122	28	61	66	104
PUG_m	92.47	101.7	8	30	62	87

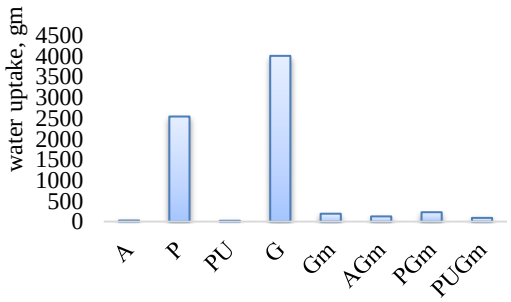

Fig.2 Water uptake of 100 g film

From the above **Fig.2,** the water uptake (swelling) of 100gm different films are shown. It is visible that the raw gelatin swelled much as expected whereas the modified gelatin absorbs only a little amount of water.

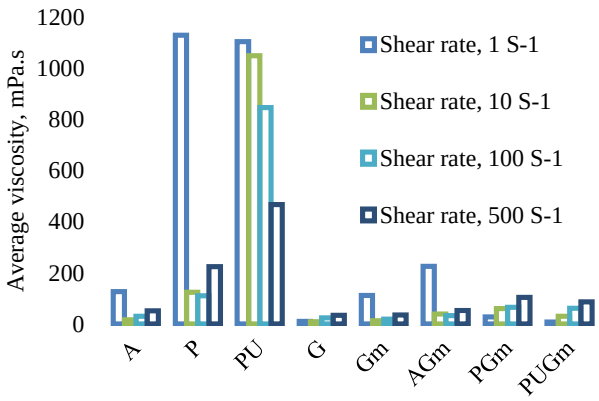

Fig.3 Average viscosity of different samples at the different shear rates.

The above **Fig.3** shows the average viscosity for different samples at different share rates. Viscosity is an important property for the binders when applied as a finishing agent on leather. Gelatin-protein (PG_m) and acrylic-protein (AG_m) blending show the reliable range of viscosity suitable for use as a finishing agent.

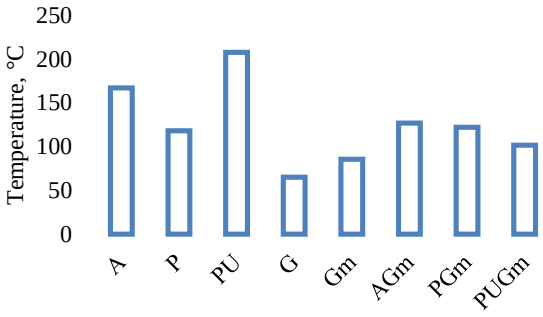

Fig.4 Comparison of thermal behavior of different samples

The above **Fig.4** shows the melting temperature of different sample films. After modification melting temperature increased for gelatin (G), and acrylic-gelatin (AG_m). However, protein-gelatin (PG_m) appears to same as the original films and PU declined sharply when mixed with the modified gelatin. The DSC analysis of original and modified films are illustrated in **Fig.5**. The onset temperatures (melting temperature) for different samples measured using these thermograms.

4. CONCLUSION

This study streamlined the utilization of leather solid waste (raw trimmings) to produce a less nonbiodegradable film without compromising performance properties of selected commercial binders except PU. It is evident that gelatin is more compatible with a protein-based binder and enhanced all the performance properties may be due to the similar chemical composition. On the other hand, acrylic-gelatin (AG_m) blending slightly differed from its original property. However, it will not create a problem in a time of application as the rheological features are within the range of acceptable limit of conventional finishing agents. This finding signifies that part of non-biodegradable commercial binders can easily be replaced partly by a biodegradable film producing modified gelatin without experiencing major changes in physical and mechanical performances. For future research, other performance property such as tensile strength, gel strength and percentage of biodegradation and glass transition property of the blended films can be determined to form a more conclusive remark. Besides, other binders such as butadiene, vinyl binders can examine in the same way. Importantly, prepared blending agents should be applied to leather and subsequently assessed for mechanical and chemical tests for verification.

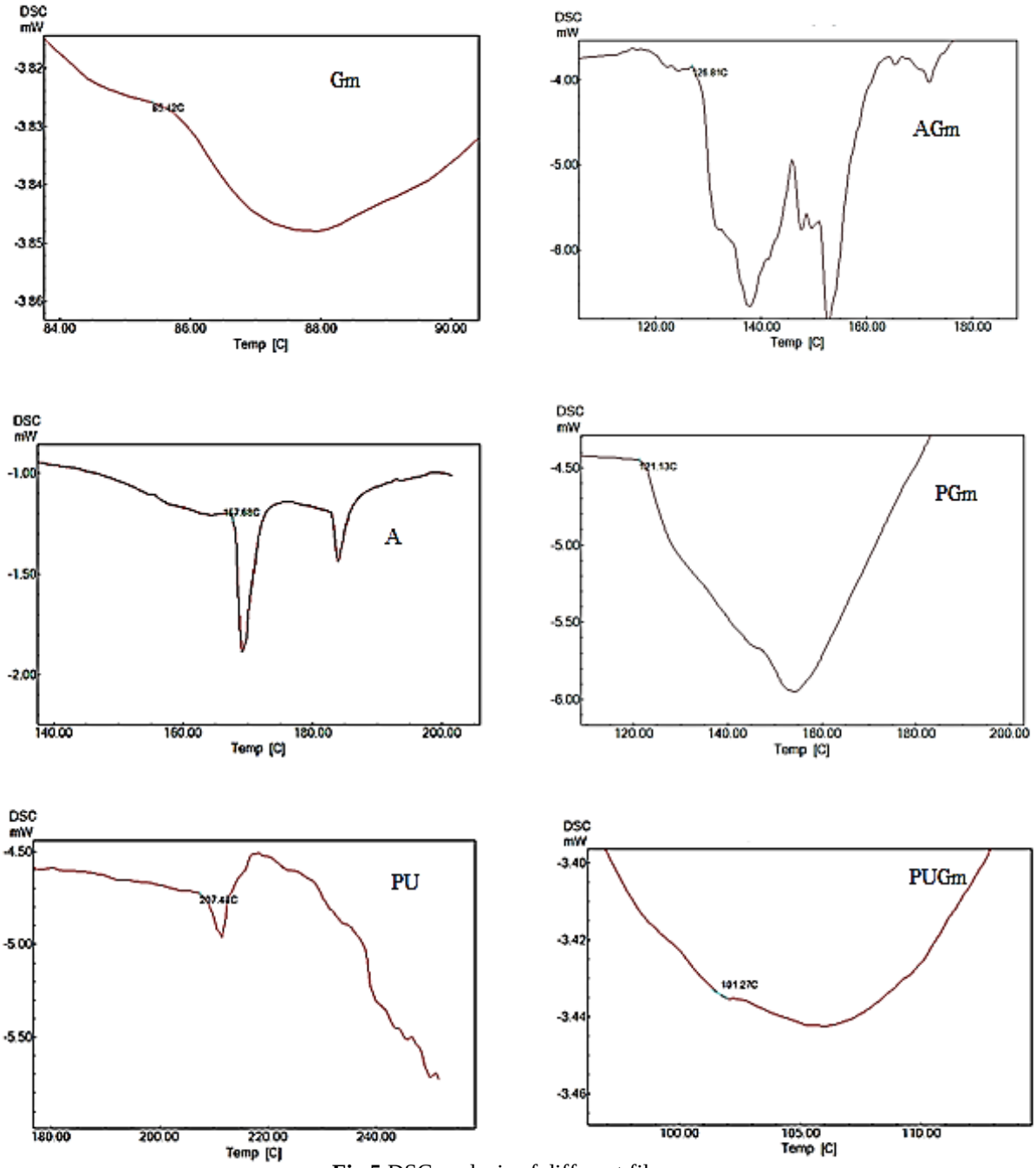

Fig.5 DSC analysis of different films

NOMENCLATURE

A	Acrylic binder
P	Protein binder
PU	Polyurethane binder
G	Gelatin
G_m	Modified gelatin
AG_m	Acrylic binder and modified gelatin blend
PG_m	Protein binder and modified gelatin blend
PUG_m	Polyurethane and modified gelatin blend

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