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Valorization of wool keratin in developing thermo-pressed plasticized films using factorial design

S. Touatou[1*], N. Belhaneche-Bensemra[1]

[1] Laboratoire des Sciences et Techniques de l'Environnement (LSTE) Department of Environmental Engineering
National Polytechnic School, El-Harrach, BP 182 Algiers–Algeria

*Corresponding author: soumia.touatou@g.enp.edu.dz ;

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ABSTRACT/RESUME

Abstract: *In this paper, wool keratin was investigated as feedstock for the production of protein-based plastics. Untreated wool fibers were thermo-pressed using glycerol as plasticizer at different levels (20 %, 30%, and 40%). Compression pressure, time and temperature were varied according to a 2^3 full factorial design. The mechanical properties were investigated by tensile measurements and discussed with respect to operating conditions. The thermal properties were studied by thermogravimetric analysis and differential scanning calorimetry. The resulting films exhibited a good thermal stability up to 150°C, a low extensibility and a maximum value of tensile strength of 20.33 MPa. It was found that the higher values of tensile strength were obtained for the films formed at the elevated temperatures investigated in this study. Additionally, Fourier transform infrared spectroscopy revealed the formation of hydrogen bonds between wool and glycerol leading to a good compatibility.*

The results showed that wool fibers can be processed into bioplastics by a thermoplastic process. Finally, the full factorial design is an efficient method for testing the influence of operatory conditions on tensile properties.

I. Introduction

Environmental problems arising from synthetic polymers have created a need for renewable feedstock to be used in biomaterial development. The use of biomass in the manufacture of polymer products contributes to reduce the impact of conventional plastics on the environment. In fact, the conversion of biomass into polymeric materials, through the use of eco-friendly processing methods, is a way to achieve sustainable development in plastic industry.

Among the natural biopolymer sources, proteins have been given much attention. Several studies have been fulfilled on the development of protein-based materials [1, 2]. In manufacturing protein-based bioplastics, thermoplastic processing is the most widely adopted method [3]. Plasticizers are often added to the protein matrix to reduce brittleness, improve processability and to modify the final structure properties [4].Glycerol plasticizer has been broadly used. It is a low molecular weight and hydrophilic plasticizer [5]. Its advantages are low cost, nontoxicity (for food and biomedical applications) and high boiling point (292 °C) [3]. From another point of view, glycerol is a by-product of biodiesel production. "Utilizing such by-products provides glycerol with an additional market driver in addition to the opportunity of improving the economics of both the biodiesel and the bioplastic industries."[3].

In this framework, wool appears as a promising material to develop bio-based plastics. Wool, described as α-keratin fibers, is a polymer made of amino acids [6, 7]. This new field allows the production of more valuable products based on biomass, and safeguards wool industry.Wool fibers are traditional raw materials used in textiles, however new applications were developed. Wool fibers were used as water filter; in building industry and as soil fertilizer [6].What fosters the use of wool fibers is their useful properties and environmental friendliness. Wool fibers are natural, renewable, sustainable, biodegradable, low carbon impact and energy efficient [7]. A clean wool fiber contains approximately 82% keratinous proteins with a high concentration of cystine, around 17% nonkeratinous proteins with low cystine content, about 1% by mass of non-proteinaceous material consisting of waxy lipids and a small amount of polysaccharide material [8].Under normal climate conditions, wool is a semi-crystalline glassy polymer [6]. Regarding the mechanical properties, wool has elongation values of 35-55 % strain, about 190-230 MPa tensile strength and 3.8-4.2 GPa Young's modulus [9].The mechanical behaviour of the fiber is affected by the moisture content. Keratin fibers have the tendency to absorb and to be plasticized by water [6].

Wool films were made in various ways through wet and dry processes. Yamauchi et al. [10] have extracted keratin from wool by reduction. A clear film was prepared from the aqueous solution of the reduced keratins mixed with glycerol. Patrucco et al. [11] have submitted wool fibers to alkali treatment and ultrasonic irradiation. Bio-composite keratin films were obtained from the cortical cells plasticized with glycerol by casting. Ramirez et al. [12] have obtained a soluble and pure keratin, extracted from wool by sulfitolysis with sodium metabisulfite. Then, the extracted keratin was converted into films plasticized by citric acid using the casting method. Mori and Hara [13] have used mechanical compression of keratin hydrogel to obtain a transparent wool film. Pavlath et al. [14] have pretreated wool fibers with different reducing agents, then films were formed by thermo-pressing without addition of plasticizers. Katoh et al. [15] have prepared keratin films by compression molding of S-sulfo keratin powder, obtained from wool by sulfitolysis and spray drying.

Several researchers have also reported the use of poultry feathers to develop keratin films. So, Barone et al. [16] have prepared feather keratin-based films by thermo-pressing, without reducing or oxidizing agents. Only glycerol plasticizer was added to the feather fibers. In another work, Barone et al. [17] have extruded feather keratin using a combination of glycerol, water and sodium sulfite. Reddy et al. [18] have produced films plasticized with glycerol from hydrolyzed and citric acid crosslinked chicken feathers by compression molding.

The present work aims at developing protein films based on wool, as a source of renewable feedstocks, that contribute to increase the diversity of products derived from biomass and reduce environmental burden, through a standard polymer processing technique, without resorting to hazard chemicals. No treatment was applied on wool to preserve the natural structure of the fibers. Compression pressure, time and temperature were varied according to a 2^3 full factorial design. The effect of plasticizer content and processing conditions on the mechanical and thermal properties of the films were studied.

II. Materials and methods

II.1. Materials

Wool fibers were obtained from sheep. They were cleaned and cut into snippets some millimeters long (about 2 mm). Glycerol used as plasticizer was purchased from VWR Chemicals (Fontenay-sous-Bois, France).

II.2. Methods

II.2.1. Films preparation

The wool films were formed by mixing the fibers with different amounts of glycerol (20%, 30% and 40% based on the weight of wool). To obtain uniform films, glycerol was first dissolved in 25 ml of distilled water. Thereafter, 5g of wool was mixed with the glycerol solution in a mortar then in a blender and dried in an oven at 55°C for 24 h. The dried mixture was placed between aluminum sheets and hot-pressed. At the end, the press was cooled by running cold water. Compression pressure, time and temperature were varied according to a 2^3 full factorial design. Thickness of the samples was measured by a micrometer and varied from 0.3 to 0.4 mm for the various conditions studied. Table 1 presents the limits of variation of the three parameters. The levels of all the studied parameters were selected based on preliminary experiments and prior knowledge from the above-mentioned works.

The formulations were coded by letters indicating glycerol content (A, B, C for 20, 30, and 40% of glycerol content respectively), followed by numbers corresponding to compression conditions in the order pressure/time/temperature according to Table1.

For example, the sample B131 designates a film having 30% of glycerol, pressed at 100 bars, for 6 min at 125°C.

Table 1. *Levels of the parameters*

Designation	Pressure (bar)	Time (min)	Temperature (°C)
1 (low level)	100	2	125
2 (center level)	150	4	135
3 (high level)	200	6	145

II.3. Samples characterization

II.3.1. Tensile Testing

Tensile properties were tested using Zwick/Roell testing machine at a rate of 10 mm/min. Films were cut in the form of strips with dimension of 100 mm×15 mm. The results were averaged from three samples.

II.3.2. Fourier transform infrared (FTIR) spectroscopy

The samples were analyzed directly by FTIR spectroscopy in ATR mode by using a Spectrum Two, Perkin-Elmer FTIR spectrometer. The spectra were collected within the frequency range 4000-450 cm^{-1}.

II.3.3. Thermogravimetric Analysis

The thermogravimetric analysis (TGA) was performed with a TA instrument (TGA Q50 V6.1 Build 181). The temperature range was from 20 to 545 °C with a heating rate set at 10°C/min under argon atmosphere.

II.3.4. Differential scanning calorimetry

DSC analysis was carried out using a Netzsch DSC 404 C apparatus. Samples were heated under nitrogen atmosphere from ambient to 300 °C at a heating rate of 10 °C/min.

II.3.5. Optical microscopy

Optical pictures of the films surface were obtained using an Optika optical microscope equipped with a camera.

II.3.6. Statistical analysis

Design of experiments was used to identify the process conditions that most impact on tensile properties. For this purpose, JMP 8.0 statistical analysis Software was used to analyze the results and to determine the most influential variables.

III. Results and discussion

III.1.Factorial design analysis of tensile properties

The tensile properties of the prepared films containing 20, 30, and 40% of glycerol, using the 2^3 full factorial design, are given respectively in Tables 2, 3 and 4. They are presented from maximum to minimum values of tensile strength.

The maximum tensile strength value is 20.33 MPa obtained from the film containing 20% glycerol and prepared at 200 bars, 6 min and 145°C (A333). 17.72 MPa and 16.04 MPa are the highest in the films with 30% and 40% glycerol respectively, formed at 150 bars, 4 min, 135°C. Compared to sample A333, the tensile strength of the film B333 is not the highest among the samples containing 30% glycerol, probably due to the higher glycerol content. Indeed, plasticizers are known to lower the minimum film forming temperature [19] and therefore the excessive temperature has probably destroyed the protein.

From Tables 2, 3 and 4, it can be noticed that the increase in glycerol content has reduced the tensile strength. Also, it can be observed that the tensile properties are temperature dependent. High tensile strength was obtained with high temperature (145°C).The low values of tensile strength were obtained at the low levels of the parameters, i.e. 100 bars, 2 min, and 125°C.

The results show that all the thermo-pressed films have low extensibility (elongation) values. A minor variation in the elongation at break is observed especially in the films containing 30% glycerol. It can be noted that elongation at break was mostly between 1.5% and 2.5%. Some values of 3% and 4% were obtained at low levels of time and temperature, that can be attributed to the presence of unmolten wool fibers.

The tensile test results are similar to that of the wool films (with a thickness of 0.3-0.4 mm) prepared by compression molding of S-sulfo keratin, where strength ranged from 7.9 to 27.8 MPa, elongation ranged from 1.1 to 4.7%, and modulus ranged from 697 to 1218 MPa [15]. The cast films prepared by Ramirez et al. [12] exhibited high elongation values (up to 600%) and tensile strength between 0.28 and 1.49 MPa (the films had a mean thickness of 0.067 ± 0.034 mm).

In order to better understand the contributions of process parameters (pressure, time, temperature), a statistical analysis was performed through a full factorial design 2^3, to study the individual effects and interactions of these variables on the tensile strength. Table 5 shows the ANOVA results for the tensile strength.

Based on these results, the correlation coefficient (R^2) is high in the first case (films containing 20% glycerol). It decreases when moving from the lower level to the upper level of glycerol content .It should be noted that droplets were observed on the surfaces of films made by 40% glycerol (after removal from the press), revealing the loss of plasticizer.

The results highlight that the only parameter with statistically significant effect in all cases is pressing temperature with a positive influence. This means that increasing pressing temperature increases tensile strength.

Table 2. *Tensile properties of the films containing glycerol at 20% in the 2^3 full factorial design*

Sample	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (MPa)
A333	2.24±0.30	20.33±0.18	1137±31
A313	2.18±0.29	17.31±2.32	1052±4
A133	1.88±0.26	16.77±2.27	1074±81
A113	1.80±0.24	15.94±0.48	1086±60
A131	1.50±0.21	14.94±2.42	1126±21
A222	1.87±0.41	12.62±1.18	1281±263
A222*	2.53±0.51	10.69±2.80	1133±95
A331	2.35±0.84	10.53±2.74	1098±54
A311	3.87±0.70	6.07±1.82	790±46
A111	4.42±1.95	4.47±1.58	744±76

*Two center points were used.

Table 3. *Tensile properties of the formulations containing 30% glycerol in the 2^3 full factorial design*

Sample	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (MPa)
B222	2.31±0.34	17.72±0.12	977±88
B222*	2.32±0.25	17.63±1.68	1008±39
B133	2.22±0.21	17.59±2.25	849±104
B131	2.37±0.07	17.29±0.66	945±57
B313	2.51±0.60	16.55±1.35	867±62
B333	2.07±0.37	16.14±1.02	754±96
B113	2.19±0.34	15.83±0.75	903±3
B331	2.37±0.72	14.89±1.97	991±81
B311	3.32±1.13	13.19±3.83	938±157
B111	4.23±1.30	11.88±0.81	780±98

*Two center points were used.

Table 4. *Tensile properties of the formulations containing 40% glycerol in the 2^3 full factorial design*

Sample	Elongation at break (%)	Tensile strength (MPa)	Young's modulus (MPa)
C222	4.43±1.15	16.04±2.10	956±31
C313	2.12±0.37	15.49±1.12	934±39
C113	1.72±0.41	15.10±2.23	1000±81
C133	1.91±0.08	14.82±0.40	963±113
C222*	2.02±0.27	14.53±3.36	1076±241
C333	1.66±0.08	11.42±1.29	762±134
C331	2.06±0.40	11.33±1.17	828±44
C111	3.59±1.30	10.04±0.56	857±76
C311	2.57±0.68	9.89±0.68	809±100
C131	3.69±1.69	9.71±1.16	798±147

*Two center points were used.

Table 5. *Analysis of variance (ANOVA) for tensile strength*

Sample	**Model coefficients**			**ANOVA results**		
	Factor	coefficient	p Value	R^2	Adj R^2	p Value
20% glycerol	Pressure (P)	-0.1759	0.6002	0.9621	0.9399	<0.0001
	Time (t)	2.4537	<0.0001[a]			
	Temperature (T)	4.7305	<0.0001[a]			
	P*t	-0.7101	0.0505			
	P*T	1.1805	0.0036[a]			
	t*T	-1.1524	0.0042[a]			
	P*t*T	0.9190	0.0157[a]			
30% glycerol	Pressure	-0.4776	0.2953	0.7332	0.5776	0.0094
	Time	1.4187	0.0069[a]			
	Temperature	1.6937	0.0022[a]			
	P*t	-0.5935	0.1989			
	P*T	0.2543	0.5708			
	t*T	-0.8221	0.0840			
	P*t*T	-0.2838	0.5277			
40% glycerol	Pressure	-0.2417	0.6742	0.6308	0.4155	0.0492
	Time	-0.4009	0.4885			
	Temperature	2.1621	0.0023[a]			
	P*t	0.0053	0.9926			
	P*T	-0.4744	0.4143			
	t*T	-0.9711	0.1090			
	P*t*T	-0.6257	0.2865			

R^2: correlation coefficient; Adj R^2: adjusted correlation coefficient
[a] Values which respond to significant tests ($p<0.05$).

On the opposite side, it seems that varying the applied pressure between the range of 100 to 200 bars does not affect significantly the tensile strength of the films ($p>0.05$), as shown in Table 5. In samples with 30% glycerol, temperature is the most important factor followed by pressing time. In samples containing 20% glycerol, the significant factors are time, temperature and their interactions. However, high levels of both time and temperature degrade the tensile strength, because of negative sign of their interaction effect coefficient (t*T). Possible explanation for this is that proteins are damaged when applying high temperature at longer pressing time.

III.2. FTIR spectroscopy analysis

FTIR analysis was carried out to investigate the interactions inside the films structure. The FTIR spectra of wool, glycerol and selected films are shown in Figure 1. Table 6 presents the characteristic peaks of the films as well as those of the native wool. The FTIR spectrum of wool shows the peptide bonds vibrations. The amide A band, which absorbs at 3282 cm^{-1} region, is related to the stretching vibration of N–H bond. The amide I band which is related to C=O stretching vibration is recorded at 1636 cm^{-1}. The characteristic band of amide II, absorbing at 1522 cm^{-1}, results from N–H bending and C–N stretching vibration. The amide III band that appears at 1235 cm^{-1}, is related to an in phase combination of N–H in plane bending, C–N stretching vibration, and to some traces of the C–C stretching and C=O bending vibrations [20, 12].

In the glycerol spectrum, the absorption band of O–H stretching is recorded at 3294 cm^{-1} and that of C–H stretching at 2934 cm^{-1} and 2880 cm^{-1}. The absorption band appearing at 1650 cm^{-1} is attributed to H_2O bending, and the C–O–H bending absorption is recorded at 1455-1418 cm^{-1}. The band registered at 1108 cm^{-1} is associated to the stretching of C–O in C2, the peak at 1031 cm^{-1} is assigned to the stretching of the C–O linkage in C1 and C3, while the three bands appearing at 994 cm^{-1}, 922 cm^{-1} and 852 cm^{-1} correspond to the vibration of the skeleton C–C [21, 22].

As can be seen by comparing the results gathered in Table 6, the characteristic peaks of glycerol still appear in the films spectra, which confirm the presence of glycerol after processing. Moreover, the major vibration peaks characteristic of proteins are maintained in the films but shifted in their position.

The shifts are observed towards lower wavenumbers for amide A and amide I peaks and towards higher values for amide II peak. For example, in amide I peak, the wavenumber decreased from 1636 cm^{-1} (wool) to 1629 cm^{-1} (sample B131) and 1624 cm^{-1} (sample B133). For amide A, the shift in wavenumber was from 3282 cm^{-1} (wool) to 3278 cm^{-1} (sample B131) and 3279 cm^{-1} (sample B133). However, the peak shifted to higher values in amide II, from 1522 cm^{-1} in wool spectrum, to 1527 cm^{-1} and 1532 cm^{-1} in B133 and B131 samples, respectively.

The observed shifts in amide A and amide I peaks reveal that NH and CO groups in keratin molecules are involved in hydrogen bonding suggesting, thus, possible interactions between keratin and glycerol through formation of hydrogen bond [23-25]. From the obtained results, it seems that the protein structure is affected by glycerol and hot pressing process, but the peptide bonds are not.

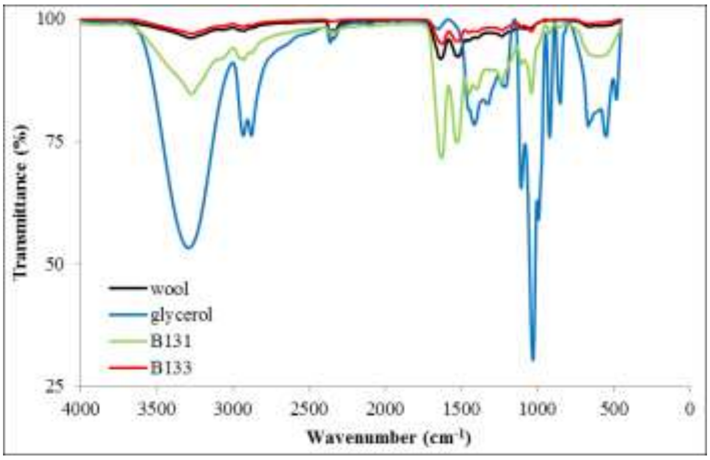

Figure 1. *FTIR spectra of wool, glycerol, samples B131 and B133*

Table 6. *FTIR spectra peak positions and assignment for wool fibers and wool films*

Region	**Peak wavenumber (cm^{-1})**			**Assignment**
	Wool	**B131**	**B133**	
Amide A	3282	3278	3279	N–H stretching
Amide I	1636	1629	1624	C=O stretching
Amide II	1522	1532	1527	N–H bending and C–N stretching
Amide III	1235	1236	1236	C–N stretching and in plane N–H bending
		1109	1109	C–O stretching at C2 in glycerol
		995	995	C–C skeleton vibrations in glycerol
		923	922	C–C skeleton vibrations in glycerol
		851	854	C–C skeleton vibrations in glycerol

III.3. Thermogravimetric analysis

TGA was performed to analyze the thermal stability of wool and wool films obtained from different operating conditions. TGA and DTG curves of the samples are shown in Figures 2 and 3. The corresponding data are given in Table 7. The TG profiles for wool shows two zones of weight loss. The first one occurs below 120°C and corresponds to the loss of humidity. The second one starts at about 153 °C and corresponds to keratin decomposition. This behavior generally conforms to the degradation pattern reported in the literature for keratin materials [26] and legume proteins [27].

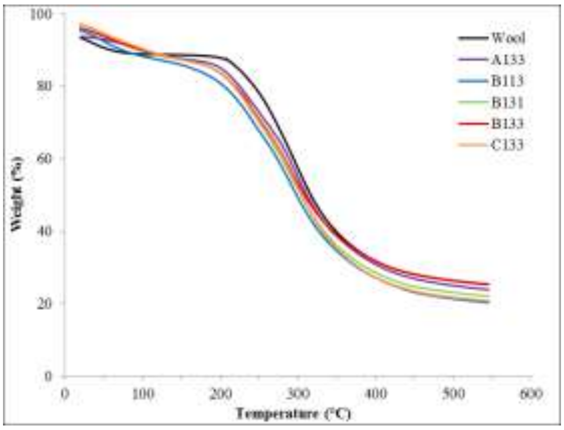

Figure 2. *TG curves of wool and selected films samples*

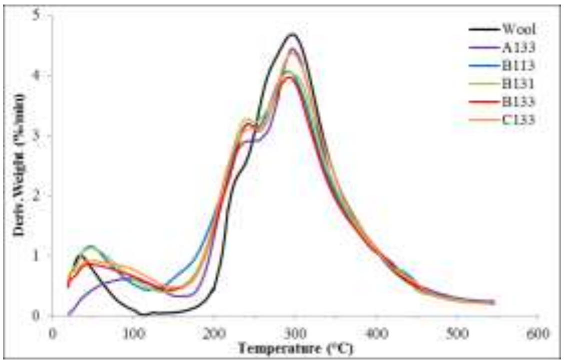

Figure 3. *DTG curves of wool and selected films samples*

The onset of thermal decomposition of wool occurs at 153 °C and the maximum in degradation rate takes place at around 296°C. So, wool might not degrade at the operating temperatures used in processing (125-145°C). Figures 2 and 3 show that the analyzed films have the same trend of weight loss, where two main stages are identified. For temperatures below 150 °C, the weight loss is ascribed to the loss of absorbed moisture. The second stage of thermal degradation, ranging from 150 to 520 °C, consists of overlapped degradation steps that are attributed to glycerol evaporation followed by protein degradation. The highest thermal degradation rate is induced by heating beyond 254 °C when the highest weight reduction is obtained. In the first stage of thermal degradation of the films, a continuous weight loss is observed on contrary to wool in which the weight loss is stabilized earlier. Furthermore, the moisture content, given by the percentage of weight loss in the first stage, is lower in wool as compared to that in the wool films (Table 7). These results show a higher hydrophilic character in the films [27], what can be related to the presence of glycerol which retains water in the material.

Comparing wool with films, wool appears to be more thermally resistant than the films samples. This can be explained by the glycerol-keratin molecular interaction which weakens the strong intermolecular bonds between keratin molecules [28] and the effect of processing. Moreover, the temperatures of maximum weight loss in the films containing 30% and 40% glycerol are shifted (Table 7). This shift is linked to some interactions between the protein and the other components that affect the thermal behavior of the protein [27] (in our case interactions with glycerol).

These results are consistent with the findings of Ullah and Wu [29] about the thermal degradation events in plasticized feather fiber films prepared by extrusion. They reported the moisture evaporation step at temperature below 150°C, the plasticizer evaporation between 150 and 250 °C, and the decomposition of keratin material at temperature beyond 250 °C.

III.4. Differential scanning calorimetry analysis

The thermal transitions of wool and wool films were studied by DSC. The thermograms are presented in Figure 4 and the results are listed in Table 7.

Table 7. *TGA and DSC data of wool and films prepared in different conditions*

	1st stage			**2nd stage**							**Total weight loss**	
Sample	T range (°C)	T_{m1} (°C)	W_1 (%)	T range (°C)	T_{m2} (°C)	W_2 (%)	T range (°C)	T'_{m2} (°C)	W'_2 (%)	$W_2 + W'_2$ (%)	$W_1 + W_2 + W'_2$ (%)	T_d (°C)
Wool	20-120	35	4.64	153-520	224	/	/	296	/	62.99	67.63	240
A133	20-153	92	6.03	164-254	229	15.88	254-520	296	47.29	63.17	69.2	245
B113	20-116	47	7.93	125-252	242	20.47	252-520	291	46.24	66.71	74.64	242
B131	20-138	48	9.31	140-251	241	18.20	251-520	293	47.19	65.39	74.7	236
B133	20-142	46	8.48	147-254	242	17.94	254-520	293	43.91	61.85	70.33	244
C133	20-145	48	9.65	160-254	248	18.38	254-520	297	48.01	66.39	76.04	246

W: weight loss (%). Tm: temperature of maximum weight loss (°C). T_d: denaturation temperature (°C).

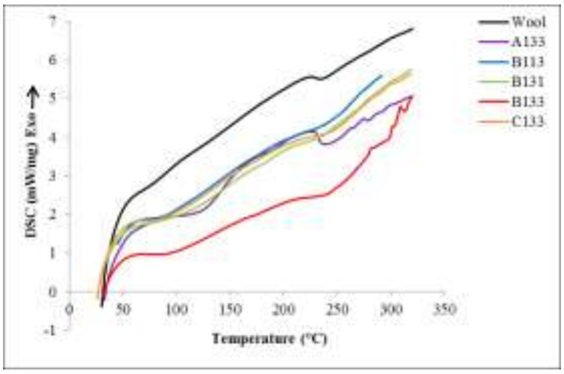

Figure 4. *DSC thermograms of wool and different wool films*

The wool fibers show two endothermic peaks, the first one is inconspicuous and broad. It appears at around 78°C and is attributed to water evaporation from the structure [30]. The low intensity of the water evaporation peak in wool suggests that the moisture content is lower in wool, which was evidenced by TGA results. The second peak is seen at 240°C and is related to denaturation of the α-keratin crystallites [30, 31].This endothermic effect is attributed to a melting-like process of the crystalline phase of wool, known in protein chemistry as the thermal denaturation temperature [6].

The result indicates that the denaturation temperature in wool is higher than the degradation temperature which onsets around 153°C. This implies that wool fibers cannot be denaturized at low moisture content without degrading, so additives must be included during their processing to promote denaturation or thermal stability [27].The processing of a plastic with acceptable performance, by molding nondenatured proteins, requires the use of a plasticizer to improve the processability and thermoplasticity of the protein [32].

The phase transition behavior in wool is similar to the previously reported ones in the investigations on the thermal properties of keratin protein derived from different sources. The endothermic peak related to the α-helix denaturation was observed at 213°C for wool [30]. It was seen at around 235°C in feather fiber [29] and around 233 °C in feather quill [33].

On the other hand, the films show a similar thermal transition behavior to that of wool fibers (Figure 4). Compared to wool, the first peak in the films is more pronounced, that can be ascribed to the presence of glycerol which helps to retain water in the material. The denaturation peak seen at 240°C in wool is also detected in the films, pointing to the conclusion that the protein material was not denatured during the process of film preparation.

It is worth mentioning that all the films formed at 145°C have exhibited the denaturation peak at higher temperatures when compared to wool. The samples A133, B133 and C133 have comparable denaturation temperatures (245°C, 244°C and 246°C respectively). However, the denaturation peak has broadened with the increase of glycerol content. In the sample B131 formed at 125°C, this thermal event was displaced towards a lower temperature (236°C). On the other hand, the most important denaturation peaks are observed in the samples A133 and B133, suggesting that a higher extent of molecular order exists in these samples [23]. The other samples are thought to be more amorphous.

The findings show that both processing conditions and glycerol content have affected the structure of wool films.

A previous study performed on keratin extrudates, from feather quill plasticized by different plasticizers, has shown a different thermal pattern, where the second endothermic peak was found at lower temperatures than the quill material. Furthermore, two peaks were detected in the glycerol plasticized materials, which were attributed to glycerol-rich and protein-rich domains [33].

III.5. Optical microscopy analysis

Figure 5 shows the surface view of the sample B222, which depicts the presence of wool fibers in the final product, highlighting that the fibers do not melt completely under processing. The resultant films seem to be like a composite made with the same raw material keratin/keratin.

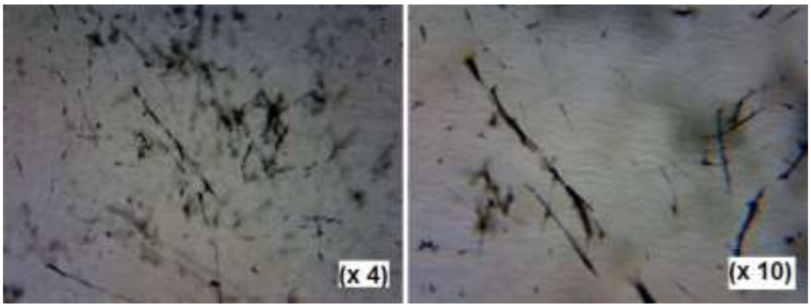

Figure 5. *Optical microscopy pictures showing the surface of a film made with 30% glycerol, pressed at 150 bar, for 4 min at 135°C*

IV. Conclusion

In the current study, wool plasticized with glycerol was processed into films by thermo-pressing. The resultant materials showed good thermal stability in the range of 50-200 °C and the wool proteins remained undenatured after processing. A good compatibility was found between wool and glycerol owing to the hydrogen bonding interactions. The addition of various amounts of glycerol had a pronounced effect on the tensile strength of the films, while the elongation at break was barely affected by the glycerol content.

Overall, it can be said that the films incorporated with 30% glycerol give good tensile properties. In fact, the tensile strength results of the samples, prepared using 20% and 40% glycerol, were similar or lower than those obtained for the films plasticized with 30% glycerol, except for the sample A333 in which the highest value was found. The full factorial design results indicate that temperature is the most important factor that significantly affects tensile strength, over the range of the selected processing conditions.

Therefore, it can be concluded that wool is a promising source of protein based bioplastics, which also implies that the other keratinous materials, especially wastes, can be processed into bioplastics with conventional techniques, thereby offering new perspectives in the field of biobased materials and wastes valorization.

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V. References

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