ALTERNATIVE SUSTAINABLE GREEN TANNING AGENTS FROM STARCH

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ABSTRACT

Two modified starches that can be used in leather production were produced by periodate oxidation and carboxymethylation methods. The selected modified samples were used in the tanning processes. The obtained results revealed that properly modified starches can be a good alternative as sustainable green tanning/retanning agents in leather production.

INTRODUCTION

Starch is an important raw material for producing sustainable green chemicals due to its features that it is an abundant, biodegradable, naturally renewable and inexpensive natural biopolymer. However, native starch cannot be used directly in leather industry due to its drawbacks. It has high molecular weight which does not allow it to penetrate within fiber structure. It is insoluble in water (a tanning material must be soluble or well dispersible in water to be transferred into fiber structure via water) and has no reactive groups that can establish stable bonds with the functional groups of collagen in order to achieve collagen stabilization and tanning effect. For these reasons, native starch must be properly modified and gain the desired properties before use in leather processing as a tanning material.[1]

MATERIALS

Native corn starch oxidized with sodium metaperiodate ($NaIO_4$) to obtain dialdehyde starch. The picked $NaIO_4$ and H_2O_2 (hydrohen peroxide) oxidized starch samples (pursuant to our earlier studies[1,2]) were carboxymethylated[3] by using monochloroacetic acid to obtain carboxymethylated starches. The remaining chemicals/solvents used in experiments were in analytical grade for each methods. In tanning experiments, pickled goat skins were used.

METHODS

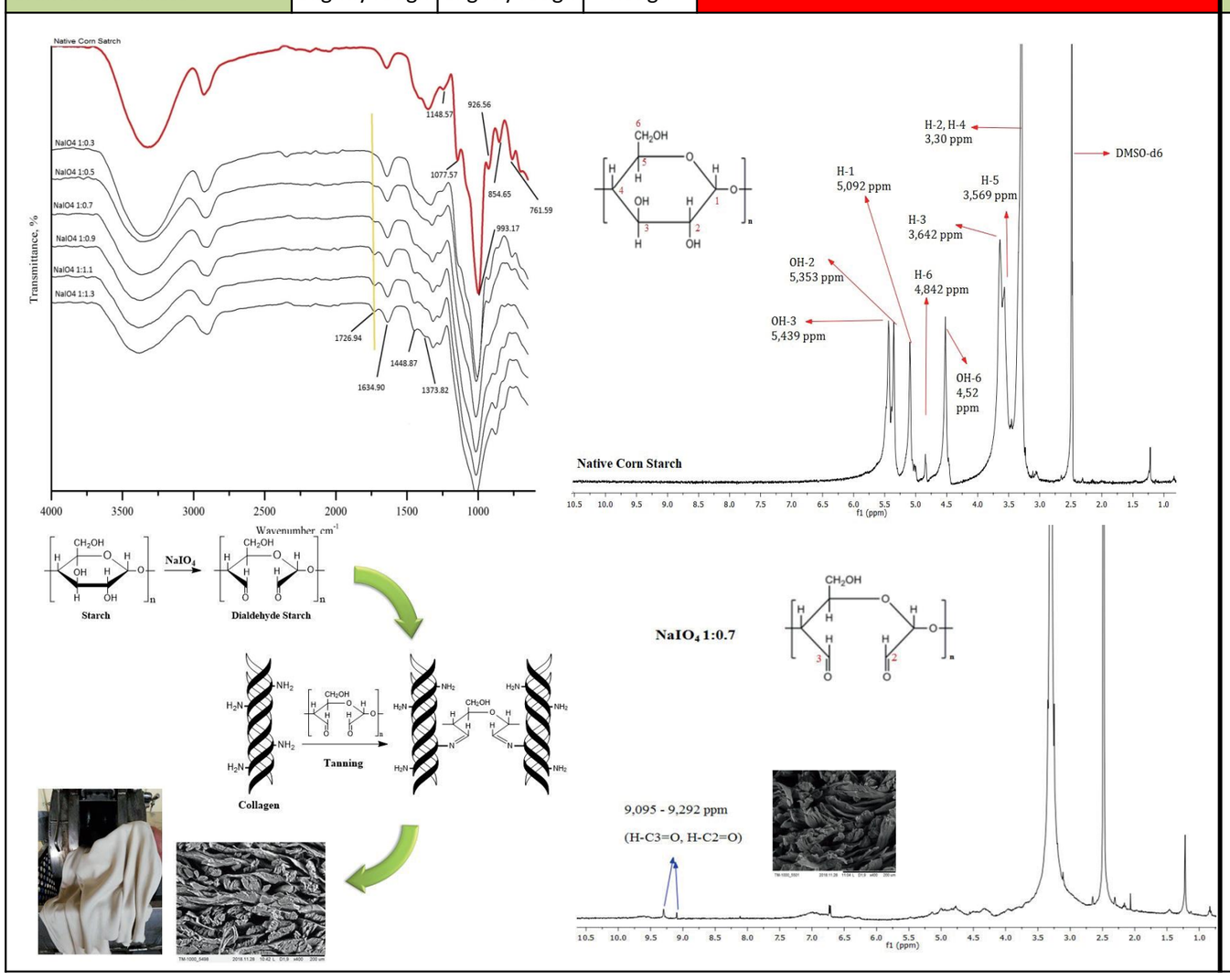
The periodate oxidation was performed as described by Zhang et al.[4] with minor change[1]. Carboxymethylation was performed in a similar way described by Hebeish et al.[5] with slight changes[3].

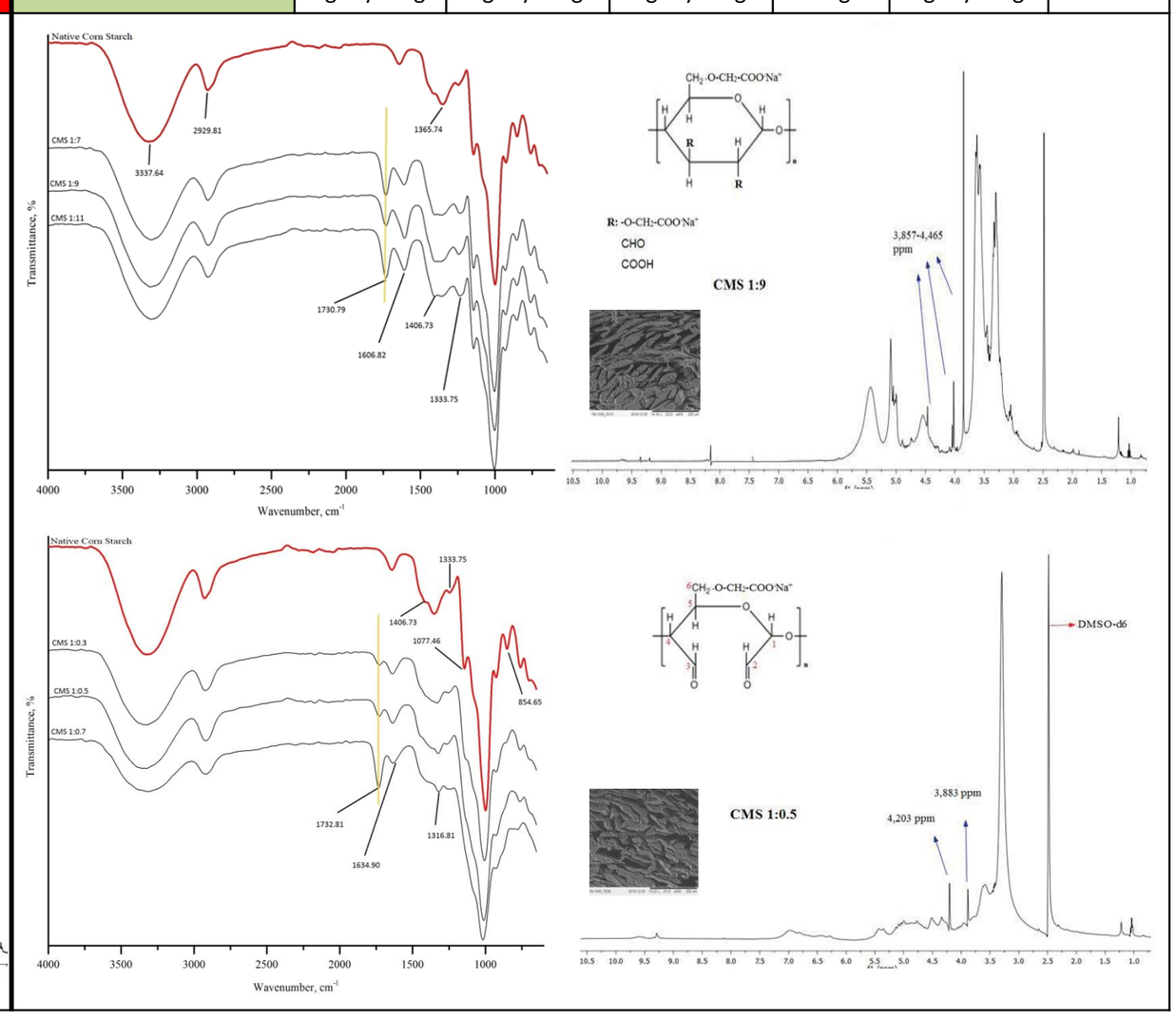
Regarding each method; product yields[2], water solubility[6] and degree of substitutions (DS)[7,8] were determined. The obtained products (dialdehyde and carboxymethyl starches) were characterized in detail by ^{1}H-NMR (MERCURYplus-AS 400 MHz spectrometer), FT-IR (Perkin Elmer Spectrum 100 FT-IR spectrometer) and GPC (Malvern Viscotek GPCMax GPC device).

Their tanning abilities were evaluated by investigating hydrothermal stabilities[9], filling[1-3] and fiber isolation characteristics (Hitachi TM-1000 table top scanning electron microscope (SEM) at 400 magnifications) and physical properties determined by mechanical tests (tensile strengths and percentage elongation[10] and tear loads[11] and organoleptically.

RESULTS AND DISCUSSION

	DIALDEHYDE STARCHES[1]							CAROXYMETHYLATED STARCHES[3]				
	From native corn starch							From H_2O_2 oxidized starch[2]			From $NaIO_4$ oxidized starch[1]	
Determination Characteristics												
Sample Name	**1:0.3**	**1:0.5**	**1:0.7**	**1:0.9**	**1:1.1**	**1:1.3**	**Sample Name**	**CMS 1:7**	**CMS 1:9**	**CMS 1:11**	**CMS 1:0.3**	**CMS 1:0.5**	**CMS 1:0.7**
Yield (%)	89,4	90,5	92,1	88,3	89,4	92,6	**Yield (%)**	67,5	49,4	48,0	91,7	85,7	82,1
Aldehyde content (%)	27,5	44,1	64,7	93,8	95,5	98,8	**DS**	0,19	0,12	0,09	0,32	0,34	0,41
Water Solubility (%)	2,4	2,9	1,8	1,8	1,4	1,6	**Water Solubility (%)**	80,6	86,5	88,2	14,8	13,3	6,8
Molecular weight (Mw(Da))	6,16K	3,68K	2,35K	18,86K	11,03K	13,09K	**Molecular weight (Da)**	Accordingly with our previous findings[1,2], H_2O_2 and $NaIO_4$ oxidation products having appropriate molecular weight/size were selected and additionally carboxymethylated.					
Polydispersity (Mw/Mn)	2,23	1,92	1,38	3,55	2,63	2,08	**Polydispersity (Mw/Mn)**						
Note: The water solubility, molecular weight and polydispersity of native corn starch was found to be 0,9%, 2.23Kx10^3 and 8,22 respectively.													
Tanning Abilities													
Filling coefficient (%)	25.7	30,6	34,6	The molecular weights of 1:0.3, 1:0.5 and 1:0.7 molar ratios are more appropriate for penetrating into the collagen fiber and picked to be used in tanning trials.			**Filling coefficient (%)**	4,2	4,9	10,5	4,7	5,5	14,0
Shrinkage temp. (°C)	69,0	70,0	73,0				**Shrinkage temp. (°C)**	52,5	54,0	54,5	65,5	66,0	67,0
Note: The shrinkage temperature of intact pelt was found to be 43,5 °C. 1:0.5 molar ratio oxidized starch sample was chosen among dialdehyde starches as having the best tanning effect and decided to be used in tanning of a whole pelt and 74,5°C of shrinkage temperature was obtained. Among carboxymethylated starches, CMS 1:0.7 sample has the best tanning effect thus a whole pelt was also tanned with this CMS sample and the shrinkage temperature of the leather was found to be 71°C.													
Mechanical Properties													
Tensile Strength (N/mm²)	35,9	26,8	17,4	-			**Tensile Strength (N/mm²)**	23,1	29,9	25,8	9,9	10,8	20,7
Elongation (%)	55,6	57,6	55,2				**Elongation (%)**	37,2	42,0	49,9	18,2	22,0	59,6
Tear Strength (N/mm)	106/0,6	103/0,8	86/1,1				**Tear Strength (N/mm)**	105,5/0,8	138,2/0,9	124,3/0,9	116,8/1	126,8/0,8	94,4/1
Note: Tanning with sample 1:0.5 of whole pelt, Tensile Strength (N/mm²): 28,2, Elongation (%). 72,9, Tear Strength (N/mm): 97,4/0,84 Tanning with sample CMS 1:0.7 of whole pelt, Tensile Strength (N/mm²): 20,88, Elongation (%). 81,48, Tear Strength (N/mm): 69,0/0,75													
Organoleptical properties of tanned leathers													
Color	Bone	Bone	Bone	-			**Color**	Beige light	Beige light	Beige light	Beige	Beige	Beige
Handle	Firm	Firm	Very firm				**Handle**	Slightly firm	Slightly firm	Slightly firm	Very firm	Firm	Firm
Grain smoothness	Slightly rough	Slightly rough	Rough				**Grain smoothness**	Slightly rough	Slightly rough	Slightly rough	Rough	Slightly rough	Smooth





CONCLUSION

The obtained results strongly encourage us regarding utilization of starch as a source for a natural based tanning agent and we think that further studies should be carried on alternative modifications.

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