MODIFICATION OF STARCH AND ITS APPLICATION IN LEATHER MAKING

JUMENG ZHEN¹ and JIANZHONG MA²

¹ Institute of Polymer Science, Zhejiang University, Hangzhou, P. R. China, 310027
² Department of Leather Engineering, Northwest Institute of Light Industry, Xianyang, Shaanxi Province, P. R. China, 712081

Summary

In this paper, the general methods of starch modification are discussed. The applications of modified starch in leather making are summarized and the potential applications of the modified starch are considered.

Though the studies of the modified starch were focussed on dialdehyde starch that has been used as tanning material in the past, the authors believe that graft starch may be a possible new material in leather making with uses as tanning agent, retanning agent, and finishing agent.

Introduction

The leather industry is continuing to improve its environmentally friendly procedures in response to legislation. As a result of such problems, even more emphasis has been given to clean production.

Starch is the chief form of carbohydrate that can be stored. Modified starch is widely used as a binding agent in paper making, food industry, spinning and weaving industry, water treatment, resin and rubber industry etc. Though its application in leather making is seldom reported, we can see its immense potential for the reasons that: (1) starch can be used in leather making if properly modified; (2) starch is abundant and is almost the cheapest industrial raw material; (3) starch is a degradable natural polymer, and it is friendly to the environment.

The Structure of Starch

Starch is composed of units of dehydrated glucose which are linked with glycoside bonds. There are two kinds of starch: straight-chain starch and branched-chain starch. Straight-chain starch is linked with −1,4 glycoside bonds and branched-chain starch is linked with −1,6 glycoside bonds. Each kind of starch has different properties according to the different contents of straight-chain and branch-chains.

From Figs 1 and 2, we can see that there are three hydroxyls in 2,3,6 placement in each dehydrated glucose unit. Among these, the primary-hydroxyl in C₆ has the strongest reactivity and then there are the secondary hydroxyls in C₂ and C₃. So there are many reactive groups in the starch molecule. Thus starch can react with different chemical reagents, the degree of reaction between starch and the chemical agent can be defined as degree of substitution (DS).

Modification of Starch

There are two kinds of methods in starch modification: physical modification and chemical modification.

Physical Modification—Physical modification refers to mixing resins and glue solution with starch in order to improve its properties. Resins used included formaldehyde polymer, isocyanate and vinyl copolymer, styrene copolymer and so on.

Chemical Modification—Chemical modification means changing the physical or chemical properties through the removal or rearrangement of molecular bonds or the introduction of other functional groups. There are many ways of chemical modification. We can choose different ways according to needs. The methods which we should mention in this paper are as follows:

Oxide Starch². Usually, oxide starch is obtained by oxidizing starch with basic hypochlorite. In the process of oxidation, the chain is split, and carboxyl and carbonyl groups are introduced. These groups prevent straight-chain starch from association. So, compared with ordinary starch, oxide starch has a lighter colour, lower viscosity and better storage properties.

Dialdehyde Starch². Dialdehyde starch is also an oxide. Usually, we use periodate acid as the oxidant. During the process of oxidation, rarely free aldehyde groups emerge. The main structure of dialdehyde starch is hemiacetal-alcohol with hemiacetal in and between molecules. As a poly-aldehyde polymer, dialdehyde can be treated as a crossing-linking agent for materials

Figure 1. Structure of straight-chain starch.
containing hydroxyl and aldehyde groups; it can be used as a tanning agent too.

**Graft Starch**

Graft starch is a new material that is widely used. In the structure of graft starch, a hydrophilic, semi-rigid chain starch is the skeleton with polyvinyls as the branches. The common monomers used include acrylic acid, acrylonitrile, acrylamide and so on. Commonly we can get graft starch by way of free radical polymerization, but the graft reaction can also be realized through a Hoffman reaction or hydrolysis reaction.

**Application of Modified Starch in Leather Making**

**Oxide Starch.** Celade *et al.* gave a new method for a chrome-free tanning process. The tanning steps are: pre-tanning with oxidized starch, tanning with titanium (Ti) salt, neutralization, retanning, dyeing, and finishing. The authors thought that pre-tanning hide with selectively oxidized starch enhanced the interaction of Ti with collagen and the leather had excellent texture and handle.

**Dialdehyde Starch and Dialdehyde Dextrin.** During the process of extraction of vegetable tanning materials, starch exists as a by-product. Torr thought that the existence of starch was disadvantage for the vegetable tanning process and that it would weaken the properties of tanned leather. He also gave a separation method for starch. Moreover, people paid attention to the character of dialdehyde starch in chrome tanning liquors.

L. del Pezzo advanced spectrophotometric methods for analysis of dialdehyde starch in tanning liquors. A. Simoncini studied the function of dialdehyde starch in chrome tanning liquors. The results showed that: (1) dialdehyde starch may act as a masking agent for a chrome tanning agent, and it can increase the stability of chrome tanning agent to basic agents. Carboxylated dialdehyde starch has stronger masking reactivity because of its high ionization; (2) the hemiacetals and carbonyl groups of dialdehyde can be reacted with Cr³⁺ and produce cross-linkages with Cr³⁺; (3) the hemiacetals and carbonyl groups can cross-link with collagen.

I. Fecher studied the possibility of using dialdehyde as a tanning agent, and pointed out that it can be used in the tannage of light leather or sole leather and can both reduce the use of other tanning agents and tanning time. E. M. Filachone *et al.* did further research on the technology of dialdehyde starch tannage. The experiments indicated that the properties and characteristics of the leather are optimum when tanning with dialdehyde starch, oxidized to the 96% level, at pH 10. A. H. Korm studied the recycling of dialdehyde starch tanning liquor, and he thought it useful in pre-tanning hides for sole leather, it can improve tanning velocity and leather properties. Y. Nayudamma *et al.* made a quantitative study on the combination of dialdehyde starch with modified collagen, and gave possible reaction mechanisms. Based on the reaction of dialdehyde starch with simple amino acids, the authors concluded that in the tanning of collagen with dialdehyde starch, the basic groups and amide groups of collagen are mainly involved. Not all the hydroxy groups in C₂, C₃ can be oxidized into aldehyde groups in the production of dialdehyde starch, and also as there is spatial hindrance in the reaction. Yiding Shen thought that tannage activity of dialdehyde starch is weaker than that of other syntans.

**Application of Modified Starch in Leather Making**

Making P. Kontio. Celda *et al.* gave a new method for a dialdehyde starch and dialdehyde cellulose. The authors contrasted the tannage properties of dialdehyde starch and cellulose. The authors thought they were similar in tanning properties, and the tanning process was similar to that of glyoxal. They also thought that the effective composition that produced the tanning property were glyoxal or similar low-molecular aldehydes that were the pyrolysis products of dialdehyde starch or dialdehyde cellulose. Shiling Wei used dialdehyde starch in the making of wet-white leather and reported that the wet-white had satisfactory qualities using dialdehyde starch alone. Lately, Sningama Pika made dialdehyde dextrin oxidized to the 87% level with periodate acid. He used the dialdehyde dextrin in tanning, and found dialdehyde dextrin penetrates into hide tissue more quickly than dialdehyde starch and had better tanning ability.

**Graft Starch.** Graft starch can be used as a finishing agent. A German patent reported that sodium carboxymethyl starch could improve the air-permeability of leather when it was used in finishing processes. Jungeng Zhen and Jianzhong Ma prepared graft starch using degraded starch and acrylamide-butyl acrylate copolymer through a Hoffman reaction between the hydroxyl and amide groups. The graft starch was used in the retannage of garment leather. The result showed that it had good performance in retanning and dyeing.

**Others.** As a hygroscopic filling agent, the use of glucose in fatliquoring can make the leather soft and prevent surface cracking in making sole leather. The product gained through the free radial graft co-polymerization of cane sugar, acrylic acid and Me₂C=C=CMeCO₂-(CH₂CH₂O)x·Me in the present of an anionic emulsification agent can be used as a filling agent. It can enhance the hygroscopic property, soften the leather and lighten the colour of leather. In another example, the mixture of anionic fatliquor, syrup or glucose, aliphatic alcohol and ammonia can be used in filling and fatliquoring in...
correct ratios. It can improve the performance of leather and increase the area of leather. Aliphatic compounds with hydroxyl groups can reduce the interaction between collagen fibres, so improving the softness of leather. Starch and glucose are the compounds with hydroxyl groups. They have an obvious softening effect on leather if properly modified.

Degraded starch can be used in making syntans. Huizhu Li succeeded in making a polyol syntan from a xylitol byproduct hydrolysate of conifer origin. The syntan is a polymer condensed with the xylitol raw material and cross-linked with an agent containing a carbonyl group. The product gave good results in furskin tanning and in combination for pig upper leather. Its tanning property came from the hydroxyl and hydroxyl methyl groups which could combine with collagen and produce a tanning effect.

Anionic starch is a material used in making wet-white leather. Anionic starch is a polyhydroxy polymer, it benefits the combination between and collagen. At the same time, because of its negative charge, electrovalent combination occurs between anionic starch and collagen or other tanning agents with positive charge. Shiling Wei et al. used anionic starch in making wet-white leather. The results showed that satisfactory wet-white can be made with the combination of anionic starch and aluminium or formaldehyde. The shrinkage temperature of wet-white leather can reach 80°C. The surface of the wet-white leather is white and the leather is full.

**Future Prospects**

From above, we can see that the research on starch is limited and the applications of starch in the leather industry is rare. The reasons that prevent the further application of starch in leather industry may exist in:

1. the molecular weight of starch is between \(10^4\)–\(10^6\), and its poor water solubility;
2. sensitive to heat, acids and bases;
3. absence of functional groups except hydroxyl groups.

We think we should decrease the molecular weight at first, and improve its resistance to heat, acids and bases at the same time and then introduce functional groups to the starch molecule.

We are interested in graft starch. Some works have been done on this subject. The product from the graft reaction of degraded starch and acrylamide-butyl-acrylate copolymer showed excellent performance in retanning. Other experimentation showed that it could take a major part in chrome-free tannage with aluminium or aldehyde though it requires further study.

A potential usage of graft starch is in finishing. The problems are in choosing the proper monomers and controlling molecular weight.

The tanning ability of dialdehyde starch has already been recognized. But preparation methods and price require attention before use on an industrial scale.

Environmental concern urges us to research on new leather chemicals. In our opinion, modified starch may be a product to benefit the economy and environment and it may be a new style of leather chemicals.

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