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Synthesis and Properties of Phenolic Syntan with HRP Catalysis

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Keywords: horseradish peroxides, gallic acid, enzymatic catalytic polymerization

Abstract. A phenolic syntan GA-SHBS had been synthesized by radical copolymerization of gallic acid (GA) and sodium 4-hydroxybenzenesulfonate (SHBS) using horseradish peroxides (HRP)/H2O2 as catalyst. The effects of monomer ratio, reaction temperature and HRP dosage on syntan were discussed. The optimum performance of GA-SHBS was got when the molar ratio of GA: SHBS is 1:1 in the presence of 5 mg HRP at 35℃ in pH 7.0. The chemical structure of copolymer was characterized by means of FTIR and NMR. The mechanism of polymerization between GA and SHBS and binding mechanism between syntans and leather fibers were proposed. The copolymer was used in making leather as tanning agent and retanning agent respectively, applied results showed that the Ts of tanned leather can reach to 75.6℃, re-tanned leather has the merits of good uniformity, fullness, softness, fine grain and non-plastic feel etc. Syntan also has good permeability, excellent tanning performance and dyeing effect.

Intorduction

Syntans are obtained by simple polymerization of organic compounds, it is widely used in leather tanning and mainly for the tight leather, and it can replace most of the vegetable tanning agent. The syntan can improve the permeability of vegetable tanning and the physical properties of leather. With the development of tanning technology, variety of syntans increased rapidly, especially the phenolic syntans. But general production process of phenolic syntans may lead to undesirable environmental effects as they can accidentally or intentionally decompose and pollution was created because of the release of formaldehyde. Meanwhile general synthesis technology was difficult to expand the transform of monomer to full extent, largely reduced the utilization rate of monomer. So it will be an inevitable trend to explore a new synthesis technology.

Enzyme is a kind of green and efficient biological material. In particular, some enzyme such as horseradish peroxidase (HRP) can be used to synthesize polymer from some monomer together with H_2O_2. There were many literatures in which the HRP/H_2O_2 was used as catalyst to prepare new copolymer with special structure using monomer such as phenols and anilines [1-4]. In this paper, copolymer GA-SHBS from gallic acid (GA) and Sodium 4-hydroxybenzenesulfonate (SHBS) was obtained by copolymerization using HRP/H_2O_2 as catalyst. Application experiments were carried out by using the copolymer as tanning agent and retanning agent, and it can enhance the physical properties and fullness of leather by adsorbing or filling in the collagen fibers [5].The chemical structure of the copolymer GA-SHBS was characterized by FTIR and NMR.

Experiment

Material. HRP was brought from Beijing Biosynthesis Co, Ltd, China. Hydrogen peroxide (H_2O_2, 30 wt %) was supplied by Tianjin Chemical Reagent No.3 Plant, China. Gallic acid, sodium 4-hydroxybenzenesulfonate, formic acid and sodium bicarbonate, all were chemical reagent and brought from Xi'an Chemicals Reagent Factory, China. Pickling pig skin and wet blue pig skin was supplied by Hebei Liushi Manufacture of leather Co, Ltd, China.

Preparation of HRP solution. The enzymatic solution was obtained by dissolving 50 mg HRP in 100 mL distilled water, and then stored in a refrigerator at 4 °C until using.