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Study on Preparation and Properties of Starch and 4-Phenolsulfonate Graft Copolymer with HRP Catalysis

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Study on Preparation and Properties of Starch and 4-phenolsulfonate Graft Copolymer with HRP Catalysis

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Abstract. Degraded starch was reacted with 4-phenolsulfonate (PHS) in water in the presence of horseradish peroxidase (HRP) catalyst/H₂O₂/acetylacetone (ACAC) to give starch and PHS graft copolymers. The structure and properties of the graft copolymer are characterized by Fourier Transform Infrared spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR). The retanned leather exhibits excellent increased thickness and softness, good dyeing ability and eligible mechanical properties.

Introduction

In recent years, more and more people pay attention to enzymatic polymerization reaction, for it not only possesses the advantages including high efficiency, high selectivity and mild reaction conditions, but also is more important that we can obtain substances with special structure and carry out chemical reaction which can't go along by means of traditional chemical reaction. For example, Simona^[1] had studied the reactivity of Horseradish peroxidase (HRP) with water insoluble phenolic compounds, and obtained a novel 4-phenylphenol ortho dimer. Lalot^[2] had studied radical polymerization of acrylamide in aqueous solution using HRP/H₂O₂/acetylacetone (ACAC) ternary system as initiator and made preliminary research on kinetics, and put forward that ACAC first generated free radical and then initiated the polymerization of acrylamide (AAM) in reaction process. Based on the research of Lalot, Cai and Sun^[3] had studied the effects of reaction temperature and initial concentrations of HRP, ACAC, H₂O₂ and AAM upon AAM polymerization kinetics catalyzed by HRP using dilatometer, and then obtained the optimum reaction conditions. Furthermore, Klivanov^[4] found some enzyme could catalyze polymerization in organic solvent, which made the application of enzyme catalysis get rid of aqueous solution. In the presence of hydrogen peroxide, HRP can catalyze acrylamide, phenols and anilines to polymerize to obtain some polymer products with special structures. It is a green preparation method^[5].

At present, the development of green leather chemicals, reducing the pollution in tanning progress and the implementing of clean production are research focus in leather industry. Starch is not only a kind of rich, biodegradable, environmentally friendly and renewable resource, but also an important green chemical material. Starch graft copolymerization is one of the main methods of starch modification, ceric ammonium nitrate or ammonium persulfate is used as catalyst in traditional starch modification, graft monomer is acrylonitrile, methacrylic acid, vinyl acetate and so on, and it's the main purpose of modification that using the modification products as water absorbent and adhesive. The chemical reaction of traditional modification method is so complicated that the properties isn't prominent when products is used as leather retanning agent^[6]. In this study, graft copolymerization of starch and 4-phenolsulfonate (PHS) will be researched with HRP/H₂O₂/ACAC as catalyst, graft copolymer with clear and simple structure will be prepared based on the efficient and specific catalytic characteristics of HRP. The structure and properties of the graft copolymer will be characterized by FTIR, NMR. Finally, the graft copolymer will be used in retanning leather.

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