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### Preparation of Grafting Starch by HRP Catalyst and its Application in Leather Tanning Process

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<b>Keywords</b>	<a href="#">Grafting Starch</a> , <a href="#">HRP</a> , <a href="#">Leather</a> , <a href="#">Tannage</a>
<b>Abstract</b>	Two grafting starch was obtained by grafting copolymerization of two synthetical vinyl monomers using HRP/H <sub>2</sub> O <sub>2</sub> as catalyst. The structure of vinyl monomers was verified by <sup>1</sup> H-NMR. The grafting polymer was proof by structures were verified by FTIR. The effect of mass ratio of starch and vinyl monomer on the grafting efficiency (GE) and grafting percentage (GP) was studied. The highest GE and GP of the first grafting starch was 35% and 32%, 59% and 50% for the second grafting starch when the vinyl monomer ratio was 9%. The molecular mass tested by GPC for the two kinds grafting starch with highest GE and GP were 54 600 and 63 970. The two mostly grafted starches were used as retanning agent. The increase ratios in thickness were 18.1% and 18.6% respectively and the tanned leather has excellent softness and flexibility.
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## Preparation of Grafting Starch by HRP System and It's Application in Leather Tanning Process

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**Keywords:** HRP; Grafting Starch; Leather; Tannage

**Abstract.** Two grafting starch was obtained by grafting copolymerization of two synthetical vinyl monomers using HRP/H<sub>2</sub>O<sub>2</sub> as catalyst. The structure of vinyl monomers was verified by <sup>1</sup>H-NMR. The grafting polymer was proof by structures were verified by FTIR. The effect of mass ratio of starch and vinyl monomer on the grafting efficiency (GE) and grafting percentage (GP) was studied. The highest GE and GP of the first grafting starch was 35% and 32%, 59% and 50% for the second grafting starch when the vinyl monomer ratio was 9%. The molecular mass tested by GPC for the two kinds grafting starch with highest GE and GP were 54 600 and 63 970. The two mostly grafted starches were used as retanning agent. The increase ratios in thickness were 18.1% and 18.6% respectively and the tanned leather has excellent softness and flexibility.

### Introduction

Starch is low cost, renewable, biodegradable and abundantly available. In recent years, modified starch aiming at improving its application properties and fields has been obtaining increasing importance. There are many methods concerning modified starch [1-7], and the grafting starch is an increasing important modification among them. The traditional initiators used in grafting copolymerization of starch were oxidants such as ceric ammonium nitrate or ammonium persulfate. The paper report a grafting starch by the catalyst of HRP/H<sub>2</sub>O<sub>2</sub> and synthetical monomers which replace the traditional monomer for HRP. The new vinyl monomers' structures were investigated by <sup>1</sup>H NMR. The structures of grafting starch were tested by FTIR. The GE and GP were tested. The properties of retanning leather with this two kinds grafting starch were studied too.

### Experimental

**Materials.** HRP, activity is 270 u/mg. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, purity 30 wt %) CR. Acetyl acetone AR. Methacrylic acid AR. Ethylene glycol AR. Citric acid AR. Sulfuric acid AR.

**Synthesis of vinyl monomer.** Methacrylic acid and ethylene glycol were added into three neck flask by the mole ratio 1:1, the esterification reaction was carried out at 100 °C for 5 hours with 4 wt% sulfuric acid as catalyst, the dosage of sulfuric acid was based on total weight of reagents. Methylbenzene was used as water extractor. The new vinyl monomer denoted as V1. The structure of V1 was characterized by <sup>1</sup>H-NMR as follow and shown in Scheme 1.

<sup>1</sup>H-NMR(400MHz,DMSO,ppm):1.9(s,3H,-CH<sub>3</sub>),2.1(S,1H,OH),3.9(t,2H,CH<sub>2</sub>),4.4(t,2H,CH<sub>2</sub>),5.6(s,1H,=CH<sub>2</sub>),6.2(s,1H,=CH<sub>2</sub>).

The equimolar citric acid based on ethylene glycol and 4 wt% sulfuric acid accounted for weight of all reagents were added to V1 to fulfill a further esterification reaction related to the synthesis of V1. The new vinyl monomer was denoted as V2. The structure of V2 was characterized by <sup>1</sup>H-NMR as follow and shown in Scheme 1.

<sup>1</sup>H-NMR(400MHz,DMSO,δ,ppm):1.91(s,3H,-CH<sub>3</sub>),2.1(S,1H,OH),4.32(t,2H,CH<sub>2</sub>),4.43(t,2H,CH<sub>2</sub>),

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