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# Carbohydrate Polymers

SCIENTIFIC AND TECHNOLOGICAL ASPECTS OF  
INDUSTRIALLY IMPORTANT POLYSACCHARIDES

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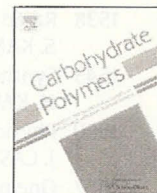
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# Graft copolymerization of acrylic acid to cassava starch—Evaluation of the influences of process parameters by an experimental design method

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## ABSTRACT

The graft copolymerization of cassava starch with acrylic acid was investigated using a free radical initiator system ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  redox system) in water. A comprehensive understanding of the important variables and their interaction has been obtained by applying an experimental design method. In this approach, two ('high' and 'low') values of selected variables are considered. Important result parameters are add-on and the grafting efficiency. Out of eight reaction variables, it was found that only temperature, starch concentration and the starch to monomer ratio have a pronounced influence on these response parameters. Moderate reaction temperature (40 °C) and high starch concentration (10%) give relatively good results of add-on and grafting efficiency. A low starch to monomer ratio favors add-on but decreases grafting efficiency. These findings can be used to optimize the production of cassava starch–acrylate copolymers and to gain insight in the process–product property interactions, for various applications.

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## 1. Introduction

The utilization of natural resources like starch and cellulose as a substitute for fossil resources derived materials is growing rapidly. To meet the product properties of many end-products, starch and cellulose modifications are inevitable. A well-established chemical modification of these polymers is graft copolymerization. For example, Stannett, Fanta, Daone, and Chatterjee (2002, chap. IX) reported that grafting cellulose (cotton) with acrylic acid, led to an increase in water absorbency of native cellulose from 4 cm<sup>3</sup>/g to 26 cm<sup>3</sup>/g. Similarly, by grafting cornstarch with acrylic acid (Hebeish, El-Rafie, Higazy, & Ramadan, 1992) the starch performed better when used as sizing agent in cotton weaving. Especially its removal after the printing process was improved, from ca. 20% for native starch to ca. 80% for the grafted starch.

Various articles on the grafting of vinyl monomers (like acrylic acid, acrylamide, acrylonitrile and also derivatives of acrylic acid, methyl acrylate, methyl methacrylate) onto natural starch have been published. More specifically, grafting of acrylic acid onto starch offers the prospect of replacing many current applications

of polyacrylic acid, by more biodegradable products based on renewable raw materials. Examples are the use as a super-absorbent polymer (Athawale and Lele, 1998, 2000; Doane et al., 2004; Kiatkamjornwong, Chomsakul, Sonsuk, 2000; Sangsirimongkolying, Damronglerd, Kiatkamjornwong, 1999; Thornton et al., 2004), as platforms for controlled drug delivery (Geresh et al., 2002), as an additive in paper and textile manufacturing (Hebeish et al., 1992; Mostofa, 1995), and as thickeners for printing cotton fabric (Bayazeed, Elzairy, & Hebeish, 1989). More recently, Willett (2009) reviewed research on starch grafting with the main focus on water-insoluble monomers.

In this paper, we report on the use of cassava starch for the synthesis of starch–acrylic acid graft copolymers. Cassava starch is abundantly available in tropical regions. In 2008 Indonesia produced over 21 million ton of cassava roots (30% of the total production in Asia) (FAO, 2008). The contribution of Asia to the total world cassava production was ca 33% at that time (FAO, 2010). A gelatinized solution of cassava starch has a low and uniform viscosity and this property facilitates processing considerably compared to other gelatinized starches.

The overall reaction scheme of the most likely reactions between starch and acrylic acid is given as structural formulas in Fig. 1. This scheme is based on a reactivity study of the oxidation of model compounds for starch and cellulose by metal ions (Mn(III), Ce(IV) and V(V) (Doba, Rodehed, & Rånby, 1984). It appeared that both the C1–C2 (end groups) and C2–C3 are predominant sites for the initiation of graft copolymerization. Most commonly, graft polymerization is brought about by free radical addition

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