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Water absorption, retention and the swelling characteristics of cassava starch grafted with polyacrylic acid

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ABSTRACT

An important application of starch grafted with copolymers from unsaturated organic acids is the use as water absorbent. Although much research has been published in recent years, the kinetics of water absorption and the swelling behavior of starch based superabsorbents are relatively unexplored. Also, water retention under mechanical strain is usually not reported. Cassava starch was used since it has considerable economic potential in Asia. The gelatinized starch was grafted with acrylic acid and Fenton's initiator and crosslinked with N,N′-methylenebisacrylamide (MBAM). Besides a good initial absorption capacity, the product could retain up to 63 g H_2O/g under severe suction. The material thus combines a good absorption capacity with sufficient gel strength. The mathematical analysis of the absorption kinetics shows that at conditions of practical interest, the rate of water penetration into the gel is determined by polymer chain relaxations and not by osmotic driven diffusion.

1. Introduction

1.1. General

Superabsorbent polymers (SAP) are materials which can absorb and retain a large amount of water or aqueous solutions. According to the Global Industry Analysts, Inc. report, it is projected that the world demand for superabsorbent polymers will reach up to 1.9 million metric tons in 2015. The fast increase in demand will be seen in the developing markets and in new applications (N.A., 2010). Superabsorbents were first developed in the US Dept. of Agriculture by grafting acrylonitrile (AN) onto corn starch and saponifying the product. Although at present superabsorbents consisting of fully synthetic polyacrylic acid dominate the market because they are cheaper to produce, research on starch-based superabsorbents is of growing interest again (Jyothi, 2010; Zohuriaan-Mehr & Kabiri, 2008). Waste disposal concern, increasing prices of petrochemical feed stocks as well as the desire to use renewable resources are driving this interest. To become more competitive, high water absorbency and higher gel strength are of great importance. The main incentive for our research project however was to find new applications of cassava starch. This is a renewable source of raw material which is abundantly available and relatively cheap in Asia, more specifically in Indonesia. Currently, the economic potential of cassava is not fully exploited which would make the development of possible industrial applications of particular interest (Witono, Noordergraaf, Heeres, & Janssen, 2012).

Superabsorbent materials consist of crosslinked hydrophilic polymer chains forming a 3-dimensional network structure. Both starch and vinyl monomers like acrylic acid, acrylamide, acrylonitrile and polyvinyl alcohol (PVA) are of interest as they contain a number of hydrophilic functionalities in their structure like hydroxyl and carboxyl groups. Ample literature reports and both older and recent patents (Chambers, 2010; Masuda, Nishida, & Nakamura, 1978) can be found on superabsorbent production based on starches, e.g. from wheat, corn or potato (Athawale & Lele, 2000; Athawale & Lele, 2001; Hashem, Afifi, El-Alfy, & Hebeish, 2005; Masuda et al., 1978; Qunyi & Ganwei, 2005; Weaver et al., 1977; Wu, Wei, Lin, & Lin, 2003). The use of cassava starch for this application is relatively novel since only few reports have appeared so far (Lanthong, Nuisin, & Kiatkamjornwong, 2006; Parvathy & Jyothi, 2012; Sangsirimongkolying, Damronglerd, & Kiatkamjornwong, 1999). Also, many papers deal with the indirect synthesis involving the grafting of starch with acrylonitrile or acrylamide followed by a hydrolysis reaction. Direct grafting of acrylic acid onto starch would eliminate the necessity of this second

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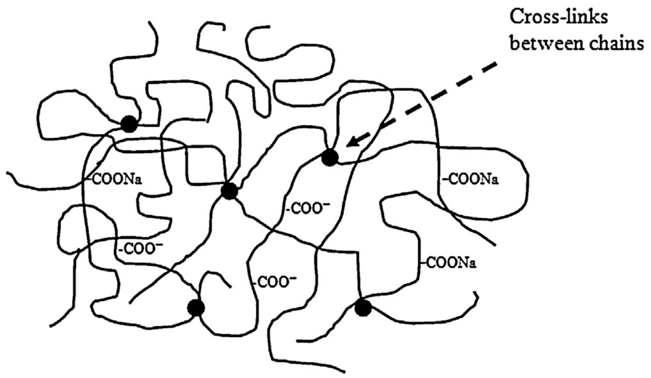

Fig. 1. Schematic view of a cross-linked polymer network (Buchholz & Graham, 1998).

process step, thus simplifying the synthetic route considerably. The process of Sanyo Chemical Industries as patented by Masuda et al. (1978) was based on this route but has not been a commercial success probably for economic reasons of the time.

In the present study, direct grafting of acrylic acid onto gelatinized cassava starch was performed in the presence of a crosslinker (N,N′-methylenebisacrylamide) using Fenton's initiation system (Fe^{2+}/H_2O_2). This initiator has the advantage of being cheap, non-toxic and of operating at mild conditions (40 °C, atmospheric pressure). Also, the system is probably easier to scale up than irradiation initiation methods like those used by Hèrold, Fouassier, and Cedex (1981) and Kiatkamjornwong, Mongkolsawat, and Sonsuk (2002). Because of the non-selective initiation, formation of acrylic acid homopolymer is inevitable. It is likely however that the polymerization crosslinker will incorporate a certain part of this homopolymer into the grafted network. The hydrogel product was analyzed to determine the efficiency of the grafting reaction. Furthermore, product properties like the capacity to absorb and retain water at different ratios of starch to monomer, various levels of crosslinking and at various degrees of neutralization were determined. A large capacity to absorb water is reported in many papers, but measuring the potential of starch based materials to retain the absorbed water under conditions that exert mechanical force on the material is a novel aspect of this work. Also, no inorganic fillers like clays were used. The method to assess the retention potential under force was newly developed.

An unexplored aspect of starch based superabsorbents is the kinetics of water absorption. The mathematical analysis of the absorption behavior results in valuable insight into the factors that determine the rate of water penetration into the gel.

1.2. Mechanisms of swelling in hydrogel copolymer

Grafting acrylic acid onto starch in the presence of a polymerization crosslinker leads to the formation of a polymer network that is loaded with negative charged –COO⁻ groups, as shown schematically in Fig. 1. Due to electrostatic repelling interactions, the chains stretch out thereby providing spaces inside the polymer networks which can absorb and retain a large volume of water or aqueous solutions, e.g. human body fluids. Moreover, the hydroxyl groups from starch and carboxyl groups from acrylic acid are hydrophilic and have a high affinity for water. The crosslinking of the polymer chains, e.g. with N,N′-methylenebisacrylamide is essential to the formation of a network in order to make the copolymer insoluble in the aqueous environment. It does restrict the expansion capability of these networks but increases the mechanical strength of the gel, which are conflicting demands in fact. From literature it is known (Buchholz & Graham, 1998) that the level of crosslinking must thus be optimized against these demands.

Neutralization by adding sodium hydroxide replaces H^+ ions of carboxylic groups by Na^+. Upon contact with water these sodium ions are hydrated which reduces their attraction to the carboxylate ions. This allows the sodium ions to move more freely inside the network, which contributes to the osmotic driving force for the diffusion of the water into the gel. As such, neutralization increases the water absorption capacity.

1.3. Kinetic analysis of water sorption: theory and literature overview

In relation with the intended application of the product as a superabsorbent, swelling kinetics is an important part of this work. When a copolymer gel is immersed in water, the water diffuses into the polymer matrix and the material starts swelling. The migration of water into dynamically formed spaces between macromolecule chains continues until it reaches the equilibrium state. Extensive reviews have been published on the mechanism of water diffusion into swellable polymers. Generally, the mathematics that governs the mass transport phenomena by diffusion is based on Fick's second law. The basic form is given by Eq. (1):

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

where C is the concentration, x the distance parameter, t the time and D is the diffusion coefficient of water into the polymer matrix.

For diffusion into a cylinder and sphere, the parameter x in Eq. (1) is replaced by the radial distance:

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial C}{\partial r}\right) \tag{2}$$

where r is the radius of cylinder or sphere.

Crank (1975) derived analytical solutions for many materials, shapes and conditions, based on Fick's law. However, he indicated that this model cannot describe the system satisfactory when diffusing molecules cause an extensive swelling of the material in which case the ability of the network to swell may become the limiting factor. That situation is characteristic for many industrial polymer superabsorbents and foodstuff applications but has not really been explored yet for starch based absorbents.

An extension of the Fick's law to compensate for this swelling, was proposed by Crank (Crank, 1975) and followed by other authors (Alfrey, Gurnee, & Lloyd, 1966; Camera-Roda & Sarti, 1990; De Kee, Liu & Hinestroza, 2005; Franson & Peppas, 1983; Frisch, 1980; Fuhrmann, 1979; Puri, Liu, & De Kee, 2008; Rogers, 1985). The mass transport in macromolecular material involves a complex process, which can be influenced among others by the internal structure of the polymer (De Kee et al., 2005; Franson & Peppas, 1983), glass transition temperature (Wikipedia, 2011), effects of swelling and relaxation and the retardation time of the polymer matrix (Puri et al., 2008), the chemical nature of the diffusing molecules (Rogers, 1985) and mechanical deformation (De Kee et al., 2005).

The diffusion behavior of water into polymers networks can be divided into three basic classes, based on the relative rates of diffusion and polymer relaxation. Case I: Fickian diffusion in which the rate of transport is much lower than the relaxation of the polymer chains. Case II: diffusion is very rapid compared with the relaxation process. Then the rate of water movement is determined by this relaxation, or the restrictions imposed by the network swelling capability. There is also an intermediate case: non-Fickian or anomalous diffusion, which occurs when the diffusion and relaxation rates are comparable. To cope with these situations, a more general model has been proposed (Bajpai & Johnson, 2005; Frisch, 1980; Űzüm, Kundakci, & Karadağ, 2006) which is in fact a severe