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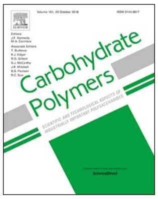

Rheokinetics of graft copolymerization of acrylamide in concentrated starch and rheological behaviors and microstructures of reaction products

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Ammonium persulfate (PubChem CID: 62648)
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Water (PubChem CID: 962)

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ABSTRACT

A widely recognized challenge in starch chemistry is to manipulate the graft copolymerization onto starch melt by reactive extrusion (REX). To understand the complex *in-situ* graft copolymerization in highly concentrated systems, we firstly used a mixer to achieve a homogeneous viscous starch melt, and then undertook dynamic rheological measurements to study the rheokinetics of the reaction. The *in-situ* synthesis also facilitated the characterization of the microstructures of reaction products. The melt mixture could be regarded to be completely micromixed since the rheokinetics was predominated by the reaction kinetics. The rheological characterization revealed that $G'$of hydrogels followed a linear progression with the crosslinker concentration. Nevertheless, the reaction temperature and initiator content had little influence on the final microstructure of hydrogels, most likely due to the strong chain transfer reaction in the melt. Additionally, high-amylose starches tended to form grafted hydrogels with a high physical crosslinking density.

1. Introduction

Hydrogels are 3D matrices constituted by linear or branched hydrophilic polymers that are chemically or physically crosslinked (Ahmed, 2015; Ullah, Othman, Javed, Ahmad, & Akil, 2015). Hydrogels have been widely applied in various fields such as medicines (Khalid, Ahmad, Minhas, & Barkat, 2017; Lam et al., 2016), engineering (Dai et al., 2017; Mohammadi, Sun, Berkland, & Liang, 2017), and agriculture (Bao et al., 2015; Elbarbary, El-Rehim, El-Sawy, Hegazy, & Soliman, 2017), due to their 3D network and unique properties. In agriculture, the hydrogels have been adopted to modify the soil environment and enhance the utilization efficiency of water and fertilizers, which contributes to the growth of crops and alleviates the damage to the environment from the leaching loss of fertilizers (Guilherme et al., 2015; Zhang and Yang et al., 2017). Moreover, encapsulation with hydrogels has been proved useful for the controlled release of pesticides for sustainable agriculture (Sarkar & Singh, 2017; Sun, Ma, Fang, Ren, & Fu, 2016). However, traditionally synthesized polymers are not biodegradable, which restricts their industrial application in agriculture. Therefore, natural polysaccharides such as cellulose (Ibrahim, Abd-Eladl, & Abou-Baker, 2015; Zhang and Luan et al., 2017), lignocellulose (El-Saied, Waly, & Basta, 2000; El-Saied, Waley, Basta, & El-Hadi, 2004; El-Saied, Basta, El-Hadi, & Waley, 2007), starch (Qiao et al., 2016; Singh, Sharma, Negi, & Dhiman, 2015), and chitosan (Kashyap, Xiang, & Heiden, 2015; Perez & Francois, 2016) have been studied for the synthesis of hydrogels, due to their abundance, biodegradability, renewability, and low cost. Starch is one of the first and most promising materials used to produce hydrogels due to its chemical

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versatility and relatively easier processability among polysaccharides (Ismail, Irani, & Ahmad, 2013; Zhang & Xu, 2017). Polysaccharide-based hydrogels are traditionally fabricated using batch processing methods such as solution, emulsion, and inverse suspension polymerization. However, these batch-processing methods are usually solvent-intensive, have low efficiency, and tend to generate significant amounts of byproducts, which have greatly restricted their industrial applications (Moad, 2011; Xie, Yu, Liu, & Chen, 2006).

During the past decades, continuous reactive extrusion (REX) has emerged as a solvent-free, cost-effective, and environmentally friendly technology to produce new materials with desired properties and added functions. Based on these advantages, REX has been introduced to the chemical processing of bio-based polymeric materials to tailor their properties, which has been known as *in-situ* REX (Formela, Hejna, Haponiuk, & Tercjak, 2017). Recently, *in-situ* REX has been successfully applied into the chemical modification, compatibilization, and functionalization of the bio-based polymers, such as polylactide (PLA) (Ojijo & Ray, 2015; Yang, Clénet, Xu, Odelius, & Hakkarainen, 2015), cellulose (Wei, McDonald, & Stark, 2015; Zhang, Li, Li, Gibril, & Yu, 2014), starch (Willett & Finkenstadt, 2015; Xu et al., 2017), lignin (Luo, Cao, & McDonald, 2016), and polycaprolactone (PCL) (Cayuela, Da Cruz-Boisson, Michel, Cassagnau, & Bounor-Legaré, 2016; Garcia-Garcia, Rayón, Carbonell-Verdu, Lopez-Martinez, & Balart, 2017). The main advantages of *in-situ* REX are the reduced costs due to a combination of polymer melting, physical blending of mixtures, and chemical reaction without purification of the final products.

It is well known that the high viscosity of polymer melt, the high shear stress involved in extrusion, and the complicated reactions between the used components, make it difficult to control the REX process precisely. All of these effects make a difference through the viscoelastic behaviors of reactive melt, which are always involved in the structural evolution during the reaction. In particular, polymer melts are usually viscoelastic and exhibit temperature-dependence and shear-dependence (non-Newtonian behavior). Therefore, the rheological behaviors of polymer melts during the REX process, known as rheokinetics, become essential in modeling REX and optimizing variable processing conditions.

Traditionally, a static mixer (torque rheometer) with a torque that is monitored has usually been used to study the rheokinetics of reaction systems with high viscosities. In particular, for polymer melts, the reaction between the polymer chains is usually controlled by the diffusion rate of mass transfer rather than the kinetics of chemical bonding mechanisms (Witono, Noordergraaf, Heeres, & Janssen, 2017; Zhou, Yu, & Zhou, 2009). However, a static mixer may not be suitable for studying all the reactions. For example, when crosslinking is involved to form a heterogeneous network, the shear stress during mixing breaks the newly formed network into large amounts of microgels due to the stress concentration effect (Cicuta & Donald, 2007; Waigh, 2016). These microgels, which are more likely to form *in-situ*, could slip between each other and thus their true viscoelasticity could not be reflected in the torque rheometer.

To address the above-mentioned issue, we utilized the graft copolymerization of acrylamide (AM) onto starch melt as the model reaction to develop a new method to study the reaction rheokinetics to guide the REX of concentrated polysaccharide systems. In this method, a modified Haake mixer was used to gelatinize and homogenize concentrated starch with the addition of required reactants, which could be regarded as *completely micromixed* to ensure a sufficient and free selectivity between the reactive groups. Then, an *in-situ* synthesis was performed in a stress-controlled rheometer through dynamic shear oscillation to study the reaction rheokinetics of starch graft copolymerization. Furthermore, the *in-situ* synthesis in a rheometer provides an incomparable benefit to allow investigating the microstructures of intact hydrogel after the chemical reaction is complete. In this way, the relationship between the reaction conditions, the graft polymerization rheokinetics, and the microstructure of the 3D network of starch-*g*-PAM hydrogels could be established for the first time.

In previous studies of the graft copolymerization of concentrated starch by REX (Carr, Kim, Yoon, & Stanley, 1992; Finkenstadt & Willett, 2005; Willett & Finkenstadt, 2003, 2006a,b,2009; Willett & Finkenstadt, 2015; Yoon, Carr, & Bagley, 1992), different reaction parameters such as the types of starch and monomer, moisture content, starch-to-monomer ratio, reaction temperature, content and type of the initiator, degree of filling, and extruder screw speed on the graft parameters of grafted starch have been fully investigated. Therefore, the effects of this wide range of reaction parameters were not the focus in this current work but we only investigated the parameters that would directly influence the reaction kinetics, microstructures, and rheological properties of the hydrogels, including the contents of the crosslinker and the initiator and the reaction temperature. Nonetheless, we used corn starches with different amylose/amylopectin ratios as model materials to further explore the effect of molecular structure on the rheokinetics of starch graft copolymerization and the microstructures of final products. As much work has been undertaken to understand the *in-situ* REX for starch-*graft*-polyacrylamide (starch-*g*-PAM), the results from this work could be compared with the previously published results to validate the feasibility of our methodology.

2. Materials and methods

2.1. Materials

Corn starches with different amylose/amylopectin ratios were used. Waxy corn starch (WCS) (amylose/amylopectin ratios: 0/100) and normal corn starch (NCS) (amylose/amylopectin ratios: 27/73) were purchased from Zhongliang Co., Ltd. Gelose 50 (G50) (amylose/amylopectin ratios: 50/50) and Gelose 80 (G80) (amylose/amylopectin ratios: 80/20) were acquired from Penford (Australia).

Acrylamide (AM) and *N,N′*-methylene-bisacrylamide (MBA) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. (China); and ammonium persulfate (APS) from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were of analytical grade and used without further purification.

2.2. Preparation of reactive mixtures

A mixing system was established based on a modified Haake Rheomix 600p twin-rotor mixer (Thermo Haake, Germany), which can provide high torque for the processing of highly viscous materials. One of the key requirements was to seal the mixer since the blending of the reactive mixtures needed to be carried out with water. The details of the modification of the mixer have been described previously (Xiao et al., 2017).

To ensure a high graft efficiency and monomer conversion in the experiment, we used optimized experimental conditions and procedures for the starch graft copolymerization, that is, the use of the initiator APS, the simultaneous initiation, and a high ratio of starch to monomer. The choice of such conditions and procedures is based on the literature. Specifically, compared with other initiators, the initiator APS could give a higher monomer conversion (Willett & Finkenstadt, 2006a). Besides, the graft efficiency decreased with the increasing ratio of acrylamide to starch (Finkenstadt & Willett, 2005). Moreover, in a concentrated system, there would be a greater possibility of chains transfer reaction, which competes with the homopolymerization (Willett & Finkenstadt, 2009). The simultaneous initiation rather than a pre-initiation process could ensure a high grafting efficiency because the completed micromixing of reactant mixtures is a prerequisite for a high reaction efficiency in the melted system (Janssen, 2004).

The reactive mixture was firstly prepared by mixing 20.0 g of starch, 10.0 g of AM, certain amounts of MBA, and 45.0 g of distilled water in the mixing chamber at 80 °C and 80 rpm, maintained for 5 min to gelatinize the starch under shear stress. Following this, the temperature of

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