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Effect of some parameters on the synthesis and the physico-chemical properties of new amphiphilic starch-g-copolymers

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ABSTRACT

The detailed studies on the graft copolymerization of phenyl methacrylate onto gelatinized potato starch in water using potassium persulfate as radical initiator were presented. The different reaction parameters such as effect of initiator concentration, starch to monomer ratio, reaction temperature and reaction time were studied in terms of grafting efficiency, grafting percent and percent homopolymer formation. It was found that grafting process of aromatic methacrylate monomer onto potato starch backbone allowed obtaining new amphiphilic copolymers with different physicochemical properties as compared to non-modified starch. The influence of the copolymer structure on the swelling behavior in polar and non-polar solvents, moisture absorbance, gelatinization properties, acid and base resistance, surface morphology and thermal properties was discussed.

1. Introduction

Starch is a high-molecular-mass, natural, biodegradable carbohydrate polymer which is mainly composed of two glucan components with different characteristic, such as linear amylose and highly branched amylopectin. This natural polymer is a major constituent of many plants such as potatoes, rice, corn, wheat, cassava, topioca, peas, beans or cereal grains, etc. (Debnath, Gayathri, & Babu, 2013; MacGregor, 2001). In recent years, polysaccharides have gained more importance and starch found wide practical applications due to its low-cost, biodegradable, availability and renewable. Starch is utilized in many branches of industry such as cosmetics, plastics, adhesives, paper, food, pharmaceutical, etc. (Bhosale & Singhal, 2006; Cova, Sandoval, Balsamo, & Müller, 2010; Kuakpetoon & Wang, 2001; Meshram, Patil, Mhaske, & Thorat, 2009; Namazi & Dadkhah, 2010; Parovouri, Hamunen, Fossel, Autio, & Poutanen, 1995; Pohja, Suihko, Vidgren, Paronen, & Ketolainen, 2004; Simi & Emilia, 2007; Whistler, BeMiller, & Paschall, 1984). However, starch has some drawbacks like highly hydrophilic nature causing their enormous swelling, brittleness, low stability in acidic environment, low moisture resistance, poor processability or incompatibility with some hydrophobic polymers. It significantly limits its use in practical applications. However, due to the presence of hydroxyl groups on the starch backbone, it is a suitable and widely studied material for the chemical modification which can extend their utility for various environmental and industrial applications. The chemical modification of starch includes many methods like hydrolysis, oxidation, esterification, etherification, crosslinking and grafting in order to introduce new functional groups into starch molecule. It causes to enhance or repress the inert properties of starch or to impact new physico-chemical properties (Bhosale & Singhal, 2006; Borsacchi, Calucci, Geppi, La Terra, Pinzino, & Bertoldo, 2014; Casas, Ferrero, & Jimenez-Castellanos, 2010; Cova, Sandoval, Balsamo, & Müller, 2010; Parovouri, Hamunen, Fossel, Autio, & Poutanen, 1995; Salimi, Yilmaz, Rzayev, & Piskin, 2014; Xu, Kennedy, & Liu, 2008; Zhang, Chen, Du, Xue, Chen, & Yang, 2015).

One of the intensively studied in recent years, techniques of chemical modification of carbohydrate polymers is the graft copolymerization. The chemical modification of starch through the graft copolymerization with hydrophobic vinyl monomers, e.g. methyl methacrylate (Aravindakshan & Kumar, 2002; Castellano, Gurruchaga, & Goni, 1997; Fakhru'l-Razi, Qudsieh, Yunus, Ahmad, & Rahman, 2001; Kumar, Ganure, Subudhi, & Shukla, 2014), ethyl methacrylate (Marinich, Ferero, & Jimenez-Castellanos, 2009), styrene (Cho & Lee, 2002; Kaewtatip & Tanrattanakul, 2008), methyl acrylate (Lutfor, Sidik, Haron, Rahman, & Ahmad, 2003), leads to the preparation of novel materials with better properties like higher rheological behavior and stability in acidic environment, higher moisture resistance, lower swelling, higher adhesion to hydrophobic polymers as compared to unmodified starches.

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Hence, hydrophobic graft modification of starch allows obtaining new copolymers with potential wide practical applications, e.g. as stabilizers, rheology modifiers, surface modifiers, compatibilizers, fillers, in coatings, as matrices and excipients for specific drug-delivery systems or as new polymeric materials, etc. (Aravindakshan & Kumar, 2002; Castellano, Gurruchaga, & Goni, 1997; Cho & Lee, 2002; Fakhru'l-Razi, Qudsieh, Yunus, Ahmad, & Rahman, 2001; Kaewtatip & Tanrattanakul, 2008; Kumar, Ganure, Subudhi, & Shukla, 2014; Lutfor, Sidik, Haron, Rahman, & Ahmad, 2003; Marinich, Ferero, & Jimenez-Castellanos, 2009).

The objective of the present work is to study the influence of initiator concentration, starch to monomer ratio, reaction temperature and reaction time on the course of the grafting copolymerization between phenyl methacrylate monomer and potato starch and the evaluation of the physico-chemical properties of obtained amphiphilic starch-g-copolymers. To our best knowledge, the formation of poly(phenyl methacrylate) chains onto gelatinized potato starch is a novel idea. We believe that the prepared materials due to their properties can find their place as low cost and more environmentally friendly stabilizers, fillers, modifiers, plastics or matrices for specific drug-delivery systems.

2. Experimental

2.1. Materials

Potato flour containing 12 wt% of water was obtained from Melvit S.A. (Poland). Methacryloyl chloride (97%) and triethyloamine (99%) were acquired from Sigma-Aldrich. Phenol (99%) was from Loba Chemie (Austria). Potassium persulfate was from Merck (Germany). Methanol and tetrahydrofuran were obtained from POCh (Gliwice, Poland).

2.2. Isolation of starch from potato flour

Starch was isolated from potato flour according to the method described in Ref. (Lim, Lee, Shin, & Lim, 1999). In a typical procedure, 50 g of potato flour and 150 mL of 0.5% solution of NaOH were placed in a glass flask equipped with mechanical stirrer and stirred (300 rpm) for 5 h at room temperature. Then, the obtained mixture was placed in refrigerator for 24 h, decanted and washed several times with distilled water to neutrality. The isolated starch was dried to a constant weight at 60 °C. Based on this procedure, it was found that the content of starch in potato flour was 85%.

2.3. Determination of amylopectin/amylose content in potato starch

The determination of amylopectin/amylose content in potato starch was carried out according to the method described in Krishnaswamy & Sreenivasan (1948). Five grams of isolated, dried starch and 300 mL of distilled water were placed in a glass flask containing a thermometer and mechanical stirrer. The suspension was intensely stirred at 60 °C for 4 h. Then it was centrifuged at 6000 rpm in order to separate water-insoluble amylopectin from water-soluble amylose. The obtained solid (amylopectin) was placed in air-dryer at 60 °C and dried to a constant weight. However, to the obtained clear water solution of amylose, 200 mL of methanol was added to precipitate. Then, precipitate was centrifuged at 6000 rpm, separated from water and dried at 60 °C to a constant weight. Based on this procedure, the amylopectin/amylose content was found to be 83/17 in used potato starch.

2.4. Synthesis of aromatic methacrylate monomer

Phenyl methacrylate monomer was prepared in our laboratory according to Grochowicz and Gawdzik (2013). In a typical procedure, 0.1 mol of phenol and 0.12 mol of triethyloamine were dissolved in 150 mL of chloroform in a three-necked glass flask. The flack was cooled down to 5 °C and then 0.12 mol of methacryloyl chloride was slowly dropped to the stirred mixture. The flask was continuously cooled in order to maintain the reaction temperature in the range of 5–7 °C. After the dropping of the whole amount of methacryloyl chloride, the reaction mixture was stirred at 5 °C for 1 h, and then at room temperature for the next 1 h. The residue formed during the reaction of methacryloyl chloride with phenol (triethyloamine hydrochloride) was separated from the solution by filtrating. The residual liquid was washed with 10% solution of HCl (100 cm^3), distilled water (50 cm^3) and 1% solution of sodium carbonate (100 cm^3) and finally with distilled water (100 cm^3). The organic layer was dried over magnesium sulfate. Then, the solvent (chloroform) was distilled under reduced pressure.

2.5. Graft copolymerization

The graft copolymerization between potato starch and phenyl methacrylate was performed in glass flask equipped with a thermometer, mechanical stirrer, reflux condenser and a nitrogen gas inlet. In a typical procedure 2.5 g of purified, dried potato starch and 50 cm^3 of distilled water were stirred (300 rpm) and heated using thermostated water bath up to temperature of 80 °C for 30 min in order to starch gelation. Then, the glass was purred with nitrogen, and the suitable amount of potassium persulfate (0.5–2 wt%) was added and mixed for next 30 min at 80 °C under nitrogen in order to form radical on the surface of starch. After 30 min, the temperature was adjusted to graft copolymerization temperature. The graft copolymerization process was performed at different temperatures (50–90 °C). The aromatic monomer was added and the reaction was continued for the next 0.5–3 h under purging the nitrogen gas in the reactor. The starch-to-monomer ratio by weight was 1:0.25, 1:0.5, 1:0.75, 1:1, 1:1.25, 1:1.5 and 1:2. At the end of the reaction, the flask contents were added to methanol (100 mL) to precipitate. The precipitate after 24 h was filtered and dried in an oven at 60 °C to a constant weight. The homopolymer was separated by Soxhlet extraction using tetrahydrofuran for 48 h. The purified starch graft copolymer was washed with methanol and dried to a constant weight at 60 °C.

The percent homopolymer formation (%H), grafting efficiency (%GE) and grafting percent (%G) were calculated using the following equations (Athawale & Rathi, 1997; Fakhru'l-Razi, Qudsieh, Yunus, Ahmad, & Rahman, 2001; Fares, El-faqeeh, & Osman, 2003):

$$\%H = \frac{\text{weight of homopolymer}}{\text{weight of monomer charged}} \times 100 \tag{1}$$

$$\%GE = \frac{\text{weight of grafted polymer}}{\text{weight of grafted polymer} + \text{weight of homopolymer}} \times 100 \tag{2}$$

$$\%G = \frac{\text{weight of polymer grafted}}{\text{weight of starch}} \times 100 \tag{3}$$

2.6. Characterization of starch-g- poly(phenyl methacrylate) copolymers

2.6.1. Fourier transformed infrared (FTIR) spectra were recorded with FT-IR spectrometer Tensor 27, Brucker (Germany) using the KBr disc technique. Sixty-four scans were collected for each