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Complex microparticulate systems based on glycidyl methacrylate and xanthan

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ABSTRACT

Porous microparticles based on glycidyl methacrylate, dimethacrylic monomers [ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate] and xanthan gum were synthesized by aqueous suspension polymerization method in the presence of toluene as diluent using two types of initiators: benzoyl peroxide and ammonium persulfate. The G microparticles based on glycidyl methacrylate and dimethacrylic monomers and X microparticles based on glycidyl methacrylate, xanthan and dimethacrylic monomers were characterized by various techniques including FT-IR spectroscopy, TG analysis, SEM analysis and DVS method. The specific surface areas were determined by DVS method, while the copolymer porosities and pore volume were obtained from the apparent and skeletal densities. The results have indicated that xanthan was included in the crosslinked matrix by means of covalent bonds. X microparticles have a porous structure with higher specific surface area (129–44 m^2/g) and higher sorption capacities compared with G microparticles (69–31 m^2/g).

1. Introduction

The selection, modification and elaboration of new materials for various applications are important criteria in the development of human civilization. Nowadays polymeric materials play an essential role in every field of human activities, taking part more and more in all the aspects of our daily existence. The increased interest of the scientific community for the polymeric microparticles is due to their properties as well as of the various requirements of medical and pharmaceutical fields.

Glycidyl methacrylate (GMA) is an attractive vinyl monomer because of its low toxicity, lower cost compared with other acrylic monomers, versatile properties and especially due to the presence in its molecule of two functional groups such as epoxy and acrylic groups, respectively (Jin, Lee, Ha, Lee, & Choe, 2007; Rahman et al., 2012).

Since the pioneering work of Svec, Hradil, Coupek, and Kalai (1975) on macroporous copolymer based on GMA and ethylene glycol dimethacrylate (EGDMA) a large number of papers have been focused on more detailed studies of the synthesis, properties, chemical modification and applications of copolymers based on GMA. Applications area of these types of copolymers is quite large, they being used as chelating ion exchangers (Malovic et al., 2007; Senkal & Yavuz, 2006), macromolecular supports for enzyme immobilization (Bencina, Bencina, Stancar, & Podgornik, 2005; Miletic, Rohandi, Vukovic, Nastasovic, & Loos, 2009; Milosavic, Prodanovic, Joranovic, & Vujcic, 2007; Vaidya, Ingavle, Ponrathnam, Kulkarni, & Nene, 2008) or adsorbents for blood detoxification (Danquah, Ho, & Forde, 2007). In literature are presented various methods to prepare porous microparticles based on GMA such as suspension polymerization (Qi et al., 2002), seeded polymerization (Kim & Suh, 2008), precipitation polymerization (Jiang & Tu, 2010), surfactant reverse micelles swelling methods (Zhou, Gu, Su, & Ma, 2007), dispersion polymerization and membrane emulsification polymerization (Wang, Zhang, Ma, & Su, 2006). Among these methods the suspension polymerization is one of the most common techniques used for the preparation of porous microparticles due to some advantages, such as: (a) small number of reagents in comparison with emulsion polymerization or other techniques; (b) lower cost compared to a broad spectrum of properties acquired by the microparticles; (c) excellent heat transfer during the process; (d) ability to control the size and size distribution of microparticles; (e) simple purification

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method for the final product (Brooks, 2010; Vivaldo-Lima, Wood, Hamielec, & Penlidis, 1997).

In suspension polymerization technique, the polymerization mixture should be adjusted according to the required properties of microparticles, especially for the achievement of the spherical shape, size and porosity. Thus, for the separation of small molecules or oligomers are used microparticles with small pores and a narrow pore distribution while for protein separation are needed porous systems which have pores with large diameters. It is known that the porosity of the copolymers is controlled by the following parameters: crosslinker and monomer concentrations, type and molar ratio of the monomers, amount and type of porogenic agent used and polymerization temperature (Malik, Ali, & Waseem, 2006; Okay, 2000). For medical applications it is very important to improve the biocompatibility and to reduce the toxicity of the macromolecular supports. A combination between synthetic and natural polymers could lead to new polymeric materials with specific properties that can be used as supports for immobilization of various biologically active molecules (Vasiliu, Bunia, & Neagu, 2009). For this purpose, the present manuscript describes a new way for the synthesis of porous microparticles based on GMA and xanthan (XAN) using the suspension polymerization technique. Xanthan gum is an anionic polysaccharide produced by *Xanthomonas campestris* and due to its nature can provide remarkable properties to the new polymeric materials in terms of lack of toxicity and good biocompatibility. In the future studies we shall continue to explore the applications of these systems as macromolecular supports for immobilization of biologically active molecules in drug delivery and biotechnological fields.

2. Experimental

2.1. Materials

Glycidyl methacrylate (Sigma–Aldrich) was distilled under reduced pressure to remove the inhibitor. Ethylene glycol dimethacrylate, diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TEGDMA) and xanthan gum were purchased from Sigma–Aldrich and were used as received.

All other reagents were of analytical grade and were purchased from Sigma–Aldrich. Benzoyl peroxide (BOP) and ammonium persulfate (APS) were used as initiators, while toluene was used as porogenic agent. Poly(vinyl alcohol) (PVA, M_w = 51.000 g/mol, degree of hydrolysis, 88%) was used as stabilizer. Ultra pure grade water was used in all experiments and has been prepared by purifying deionized water ($\Omega < 10^{-6}$ S/cm) with Millipore Simplicity-UV apparatus.

2.2. Preparation of copolymer microparticles

2.2.1. Synthesis of G microparticles

The microparticles based on GMA-EGDMA, GMA-DEGDMA and GMA-TEGDMA labeled G microparticles were prepared by aqueous suspension polymerization in a cylindrical reactor with a volume of 500 cm^3. The reaction mixture consists of two phases:

a) Aqueous phase consisting of distilled water as a dispersion medium and 1.5 wt.% PVA as suspension stabilizer.
b) Organic phase consisting of GMA (90 mol%), crosslinking agents [EGDMA (10% and 20% mol, respectively), DEGDMA (10 mol%), TEGDMA(10 mol%)], free radical initiator (BOP) (2.5 wt.% with respect to the total amount of the monomers) and toluene as porogenic agent [D = 0.5, where D = ml toluene/(ml toluene + ml monomers)]. The inert porogenic agent must be soluble in the monomer mixture but insoluble in the continuous phase of suspension polymerization.

2.2.2. Synthesis of X microparticles

The microparticles based on GMA-EGDMA-XAN, GMA-DEGDMA-XAN and GMA-TEGDMA-XAN, labeled X microparticles were obtained through the same procedure with few modifications:

1. The aqueous phase was formed by a solution of PAV and xanthan (1.5 wt.%).
2. In the aqueous phase a second free radical initiator (APS) is used to create radicals on polysaccharide chains. The XAN/monomers ratio was 1:23 (w/w) and (BOP + APS) content was 2.5 wt.% with respect to the total amount of monomers.

For all experiments the organic/aqueous phase ratio was 1:9. The copolymerization reactions were conducted under N_2 atmosphere for 8 h at 78 °C and 1 h at 90 °C with a stirring rate of 360 r.p.m.

Both sets of copolymers with and without XAN obtained in beaded form were separated by decantation, washed with hot water and then were extracted with methanol in a Soxhlet apparatus in order to remove traces of residual monomers and porogenic agent.

Finally, the G and X microparticles were dried under vacuum at 50 °C for 48 h and sieved.

2.3. Characterization of microparticles

The epoxy group content was determined by titrimetric method namely HCl-dioxane method (Vogel, 1958, Chapter XXXVIII). Simultaneously, epoxy group content in the structure of copolymers was determined by FT-IR analysis on the basis of a calibration curve using the peak areas at 908 cm^{-1} and 1717 cm^{-1} (Bakhshi, Zohuriaan-Mehr, Bouhendi, & Kabiri, 2009; Canto & Pessan, 2002).

FT-IR spectra were obtained on a Bruker Vertex FT-IR Spectrometer, resolution 2 cm^{-1}, in the range of 4000–400 cm^{-1}. In order to obtain the FT-IR spectra, a known quantity of microparticles (0.03 g) was mixed and ground with potassium bromide.

The thermal degradation of microparticles was performed in a METTLER 851 Derivatograph, carried out using 4 mg of sample and heated at a rate of 10 °C/min under nitrogen atmosphere. The weight loss versus temperature was recorded.

The number average diameter (D_n) and the particle size distribution of G and X microparticles were achieved using the principle of laser diffraction (Laser Diffraction Particle Size Analyzer WingSALD 7001).

The specific surface area of the microparticles was determined using the Brunauer, Emmet and Teller (BET) method (Ng & Mintova, 2008) using the fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK).

The apparent (ρ_{ap}) and skeletal (ρ_{sp}) densities of microparticles were measured by pycnometric methods with mercury and heptane, respectively (Seidl, Malinsky, Dusek, & Heitz, 1967; Vlad & Vasiliu, 2010). The pore volume (PV) and the porosity (P) of microparticles were calculated as follows:

$$\mathrm{PV}\ \ (\mathrm{mL/g}) = \frac{1}{\rho_{ap}} - \frac{1}{\rho_{sp}} \tag{1}$$

$$\%P = 100 \cdot \left(1 - \frac{\rho_{ap}}{\rho_{sp}}\right) \tag{2}$$

Sorption–desorption isotherms were registered with fully automated gravimetric analyzer IGAsorp produced by Hiden Analytical, Warrington (UK). The weight change was measured with an