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Synthesis and characterization of hydrogels from 1-vinylimidazole. Highly resistant co-polymers with synergistic effect

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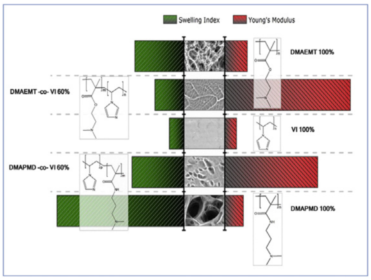
HIGHLIGHTS

- Highly resistant materials with improved mechanical properties can be obtained by adding 1-vinylimidazole as co-polymer.
- A synergistic effect can be observed by the combination of hydrophilic and hydrophobic monomers.
- The mechanical and swelling properties of different materials obtained were determined.

GRAPHICAL ABSTRACT



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ABSTRACT

Monomers N, N-(dimethyl) amine ethyl methacrylate (DMAEMT) and N-[3 - (dimethylamine) propyl] methacrylamide (DMAPMD) were co-polymerized with 1-vinylimidazole (VI) in different proportions and crosslinked with N,N′-methylenebisacrylamide (BIS) in aqueous phase, to yield highly resistant hydrogels. The polymeric products were studied by swelling kinetics, solvent diffusion within the crosslinked network, thermal decomposition, *infrared spectroscopy* (*FTIR*), *variable pressure scanning electron microscopy* (*VP-SEM*), *and* mechanical and rheological tests. The incorporation of VI in the polymerization reaction led to beneficial changes in the properties of the final materials *such* as improvement in the resistance of the materials and increase in the percentage of deformation capable *of withstanding elongation before breaking. All VI-containing products were mechanically strong with* respect to homo-polymers (DMAPMD 100% and DMAEMT 100%). The most resistant products were DMAPMD-co-VI 60% and DMAEMT-co-VI 60%. A synergistic effect with the addition of VI is revealed by Young's modulus that *increases 5 and 10 times regarding the hydrogels yielded from pure monomers, respectively.*

1. Introduction

Functionalized polymers can be obtained by co-polymerization of monomers having different functional groups, or by post-modification of formed products in polymerization reactions [1–7]. Functionalized hydrophilic crosslinked materials capable of absorbing large amounts of water and containing functional groups (carboxylic acids, amines, hydroxyls, etc.) have been promising in their application as controlled-release systems for drugs, mechanical actuators, supports for tissue engineering, biomembrane systems, biosensors, chromatographic supports, metal ion complexing agents [8–12], among others. The application of these materials is sometimes restricted due to poor mechanical properties [13–15]. It mostly consists of water, which does not contribute to the

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mechanical strength of the gel. Due to their high water-holding capacity, polymer chains are widespread with low capacity for responding to an applied force, turning into particularly fragile materials [16–18]. However, the strength of the hydrogels can be improved by using different strategies. Some consist of increasing the density of crosslinks [19] or adding hydrophobic monomers to the polymer architecture [20], in order to generate higher-density areas or a larger amount of intermolecular interactions that contribute to increasing the module or stiffness of the hydrogels [21,22]. These modifications result in reducing the amount of water absorbed, for which compositions should be formulated by compromise between optimization of hydrophilicity and excellent mechanical properties [17]. For instance, gelatin films were stabilized by crosslinking with natural crosslinker genipin [23]; nano-sized attapulgite fibril was used to enhance the mechanical properties of polymeric hydrogels [24]; 2-vinyl-4,6-diamino-1,3,5-triazine was used in a co-polymerization to strengthen the mechanical properties of the hydrogel formed by self-hydrogen bonding of diaminotriazine [25]; ionically crosslinked alginate and covalently crosslinked polyacrylamide were mixed to yield extremely stretchable and tough hydrogels [26]; poly-(2-acrylamido-2-methyl-1-propane sulfonic acid) was combined with polyacrylamide [27] to yield double-network with excellent mechanical properties [28].

Other alternative to reinforce the structures of the hydrogel is the use of aromatic functional groups (in the constitutive monomers). In these systems, aromatic interactions play an important role [7] in maintaining the mechanical properties of the resulting hydrogels due to the rigidity of the backbone and the hydrophobicity of the aromatic segment [29]. Hence, obtaining a crosslinked structure with high strength, stiffness and toughness to resist failure would be advantageous over currently used materials [6,30–32].

1-vinylimidazole (VI) is a monomer with promising properties for modification of hydrogels [33]. Its aromatic structure and pH response have attracted the attention of researchers for numerous applications such as catalytic agent, metal-ion complexation, counter ion and dye binding [34,35]. Most of these applications have been tested with linear [36–41] and crosslinked polymers, using, however, VI as the constitutive monomer [42–46]. In addition, VI has not been almost used in those types of networks as a modifier capable of improving the texture or mechanical properties of the final materials [47]. The incorporation of VI into hydrogel structures has been regularly used especially in the formation of polymer-metal complexes used as immobilized catalysts [48–51].

The use of acrylate and acrylamide-based monomers is widespread in crosslinked materials [52]. In particular, 2-(dimethylamino) ethyl methacrylate (DMAEMT) and N-[3-(dimethylamino) propyl] methacrylamide (DMAPMD) are quite similar, except in their functionality (ester and amide, respectively). Hence, DMAEMT acts as a hydrogen-bond acceptor and DMAPMD acts as both hydrogen-bond acceptor and donor [53]. The aim of this paper thus focused on the analysis of the changes on properties based on the different possible interactions with VI, which could maximize structural freedom in highly steric environments [54].

Now, in general, of all possible applications, the use of hydrogels as complexing metal ions is highlighted since, once the polymer-metal complex ion is obtained, these can be used as supports for the immobilization of biomolecules, such as enzymes [55]. In turn, the study of ligands and polymers with supported metal complex derivatives is relevant in the field of catalytic and bio-organic chemistry [25].

Thus, the objective of the present study was the preparation of crosslinked hydrophilic co-polymers with specific functional groups in their structures using DMAPMD, DMAEMT and VI as monovinyl monomers and N,N'-methylenebisacrylamide (BIS) as a crosslinking agent. Different proportions of VI were incorporated into the polymer structures in order to yield mechanically strong hydrogels. A complete physico-chemical characterization of all the products was carried out with the purpose of using them in metal ion retention in future works.

2. Material and methods

2.1. Reagents

The following chemicals were used as purchased: N,N-dimethylaminoethyl methacrylate (DMAEMT; Sigma); *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMD; Aldrich); 1-vinylimidazole (VI; Aldrich); N,N'-methylenebisacrylamide (BIS; Sigma); ammonium persulphate (APS, Anedra); N,N,N′,N′-tetramethylethylenediamine (TEMED; Anedra); glacial acetic acid (CH_3COOH, Cicarelli); phosphoric acid (H_3PO_4, Cicarelli); boric acid (H_3BO_3, Cicarelli) and sodium hydroxide (NaOH, Cicarelli). Britton Robinson (BR) buffers were prepared according to reference [56]. The pH of each solution was adjusted at 3.02, 5.01, 7.00, 9.00 and 11.06.

2.2. Hydrogel synthesis

All matrices were prepared by free-radical cross-linking polymerization. The procedure for co-polymerization can be described as follows: monovinyl monomers (DMAEMT; DMAPMD and VI) and cross-linker (BIS) were dissolved in 4 mL of Milli-Q water in glass test tubes. The solution was mixed for 5 min and sonicated until complete homogenization. The polymerization solution was deoxygenated with N_2 for 5 min. To initiate the polymerization reaction, APS and 50% aqueous solution of TEMED were added to the reaction mixture and transferred to disposable syringes. The reaction was allowed to proceed for 1 day at room temperature. The synthesized hydrogels in rod form were cut into discs and thoroughly washed with Milli-Q water. They were then dried until constant weight. Table 1 summarizes the experimental conditions to prepare the hydrogels, and Fig. 1 shows monomer structures. The final products were named DMAPMD 100%; DMAPMD-co-VI 20%; DMAPMD-co-VI 60%; VI 100%; DMAEMT 100%; DMAEMT-co-VI 20% and DMAEMT-co-VI 60%, depending on molar co-monomer composition.

2.3. Swelling properties: dynamic, equilibrium and pH-response studies. Cycles of swelling and deswelling

The swelling indexes in equilibrium, q_w, were determined according to Eq. (1) where M_s and M_d are the mass of water-swollen hydrogel at equilibrium and the dry mass, respectively. To register

Table 1
Experimental conditions for the synthesis of hydrogels.

Hydrogel[a]	DMAPMD (mol 10^{-3})	DMAEMT (mol 10^{-3})	VI (mol 10^{-3})
DMAPMD 100%	5.60	–	–
DMAPMD-co-VI 20%	4.48	–	1.12
DMAPMD-co-VI 60%	2.24	–	3.36
VI 100%	–	–	5.60
DMAEMT 100%	–	5.60	–
DMAEMT-co-VI 20%	–	4.48	1.12
DMAEMT-co-VI 60%	–	2.24	3.36

[a] BIS: 1.1 × 10^{-3} mol; APS: 0.0128 g; 50% aqueous solution of TEMED: 0.5 mL; water: 4 mL.