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Original article

Modified gelatin with quaternary ammonium salts containing epoxide groups

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ABSTRACT

An EPDDMAC-GE polymer (hydrophilic molecule) has been synthesized based on epoxypropyl dodecyl dimethyl ammonium chloride (EPDDMAC) and gelatin. A DEEPSAC-GE polymer (hydrophobic molecule) has been synthesized based on diethyl-2,3-epoxypropyl-[3-methyldimethoxyl] silpropyl ammonium chloride (DEEPSAC) and gelatin. Compared with initial gelatin, the gelatin modified with quaternary ammonium salts containing epoxide groups exhibits stronger antibacterial activity.

1. Introduction

Gelatin is derived from the waste, or by-products, of manufacturing processes comprising tannery, pharmaceutical and food segments. It can be taken as a renewable and biodegradable material [1,2]. However, its applications are limited in many areas due to its poor antibacterial activity, brittleness and poor water solubility. Chemical grafting or cross-linking of gelatin is an effective way to introduce stable covalent bonds between protein segments to improve the chemical and physical properties of natural polymers [3–5]. The epoxy compounds are commonly used in modified research.

Vargas *et al.* [1] studied the cross-linking of gelatin by ethylene glycol diglycidyl ether (EGDE). The best cross-linking reaction between gelatin and EGDE was achieved at pH9 and an EGDE concentration of 10 wt%. The cross-linking structures were confirmed by FT-IR and ^{13}C NMR techniques. Xu *et al.* [6], studied the microstructural transformations of PGG polymers which were based on α-[3-(2,3-epoxy-propoxy)propyl]-ω-butylpolydimethyl siloxanes (PDMS-E) and gelatin induced by sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS). The results indicated that the microstructural transformation of PGG was determined by the compatibility of the two polymers in anionic surfactant aqueous solution and the chemical nature of their monomers.

In the present work, chemical modification of gelatin by epoxypropyl dodecyl dimethyl ammonium chloride (EPDDMAC) and diethyl-2,3-epoxypropyl-[3-methyldimethoxyl] silpropyl ammonium chloride (DEEPSAC) at varying the gelatin concentrations in water is studied. The grafting density of epoxy quaternary ammonium salts grafted gelatin polymers is investigated using the Van Slyke method by measuring the conversion rate of free NH_2 groups of gelatin [3]. The structure of modified gelatin is characterized by FT-IR, ^{13}C NMR and elemental analysis. The glass-transition temperatures T_g, contact angles and antibacterial properties are reported.

2. Experimental

The grafting route of EPDDMAC-GE was depicted in Scheme 1. Gelatin (type A obtained from pigskin, having an approximate molecular weight of 50,000 and isoelectric point at pH8 determined by fluorescence measurements) was dissolved in distilled water (8%, w_s/w_g), and after 5 h, the gelatin solution was heated to 50 °C to ensure complete dissolution. The pH of the solution was adjusted to 10.0 by NaOH (2.0 mol/L) solution [7]. The EPDDMAC (laboratory-made compounds, mp. −0.28 °C,

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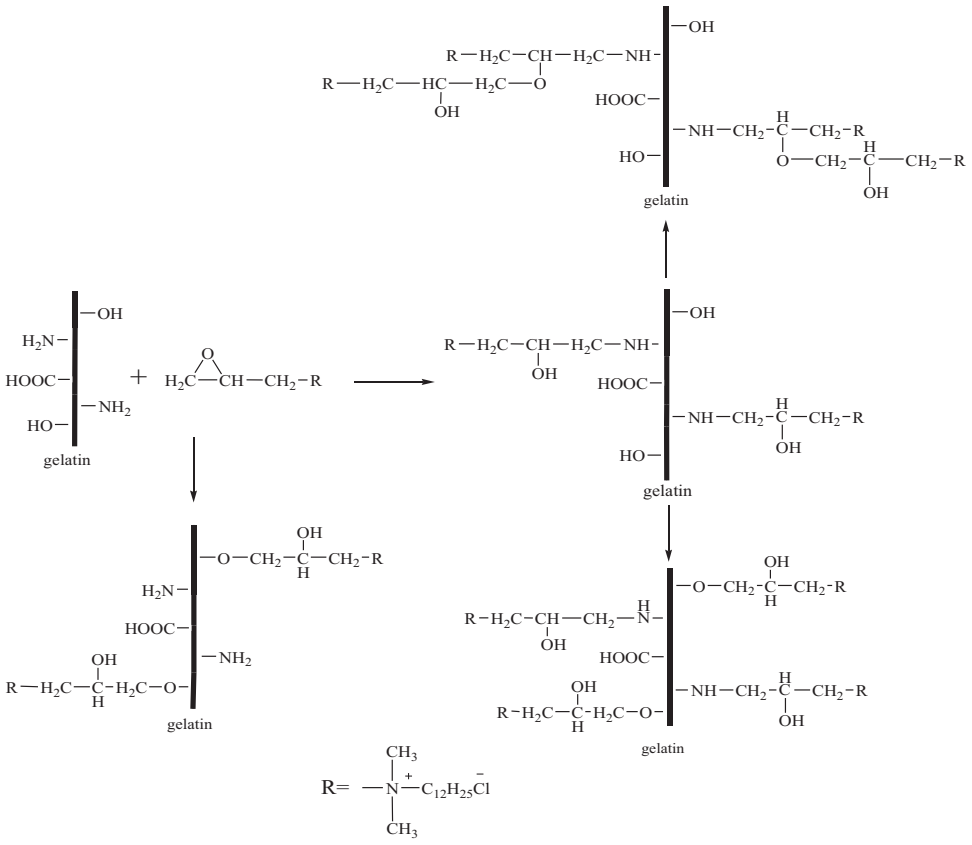
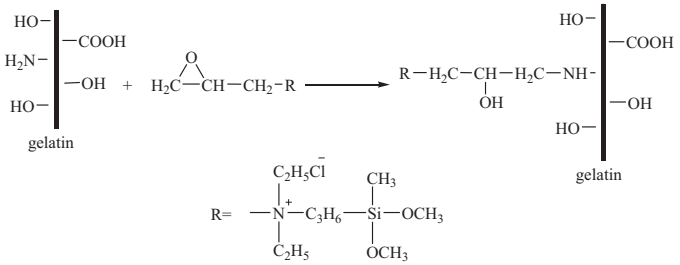


Scheme 1. The synthetic routes of EPDDMAC-GE polymers.

purity 98.6%) with predetermined epoxy groups/amino groups (1:1, mol:mol) was then slowly added to the gelatin solution at 50 °C with stirring. After reacting for 5 h, the solution was cooled to 5 °C and the content of free $-NH_2$ groups was determined by the improved Van Slyke method at 40 °C [8]. The grafting density of $-NH_2$ groups reached 40.03%. The grafting route of DEEPSAC-GE was depicted in Scheme 2. Gelatin was dissolved in distilled water (6%, w_s/w_g), and after 5 h, the gelatin solution was heated to 55 °C to ensure complete dissolution. The pH of the solution was adjusted to 11.0 by NaOH (2.0 mol/L) solution. The DEEPSAC (laboratory-made compounds, purity 98.9%) with predetermined epoxy groups/amino groups (1:1, mol:mol) was then slowly added to the gelatin solution at 55 °C with stirring. The conversion of $-NH_2$ groups reached 42.15%. All samples were freeze dried at −50 °C for 24 h and extracted by acetone for 72 h [6]. The chemical structures of the gelatin and its derivatives were determined by FT-IR spectra (Nicolet NEXUS 470 FT-IR spectrometer), ^{13}C NMR spectra (Bruker Advance 400 spectrometer) and elemental analysis (Vario EL III, Elementar Analysen System GmbH, Germany).



Scheme 2. The synthetic route of DEEPSAC-GE polymers.

3. Results and discussion

Milch [9] investigated any indications of gross changes in the infrared spectra of the gelatin system with gel melting. In this study, the chemical structures of the gelatin and its derivatives were also determined by the infrared spectra. Fig. 1 is the infrared spectra of three polymers. Comparing the spectrum of EPDDMAC-GE (b) with the spectrum of gelatin (a), the absorption band at 1643 cm^{-1} (belonging to the N–H deformation of primary amine groups on gelatin chains) nearly disappeared, implying that the

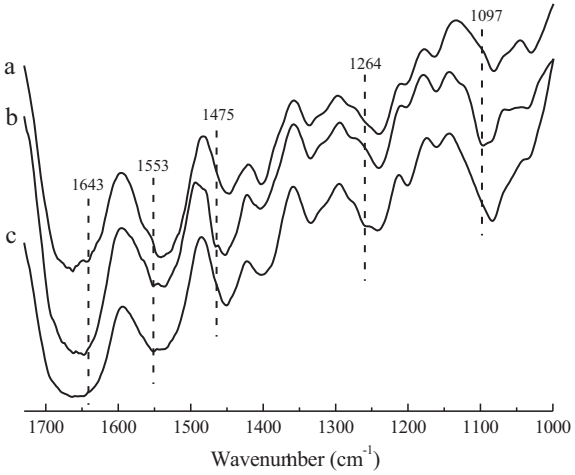


Fig. 1. The FT-IR spectra of (a) initial gelatin, (b) EPDDMAC-GE and (c) DEEPSAC-GE.