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European Journal of Pharmaceutics and Biopharmaceutics 67 (2007) 690–698
European Journal of Pharmaceutics and Biopharmaceutics
www.elsevier.com/locate/ejpb

Research paper

Enhanced enteric properties and stability of shellac films through composite salts formation

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Received 25 January 2007; accepted in revised form 11 April 2007
Available online 20 April 2007

Abstract

The objective of this study was to improve the properties of shellac by composite salts formation. The shellac samples were prepared in various salt forms by dissolving them with 2-amino-2-methyl-1-propanol (AMP) and ammonium hydroxide (AMN) at various ratios of AMP:AMN. The results demonstrated that aqueous solubility of the shellac salts was improved as the ratio of AMP:AMN increased. The absorbance ratio of the FTIR peaks assigned to C=O stretching of carboxylate and carboxylic acid (ABS_{1556}/ABS_{1716}) was increased with the increase of the AMP fraction, suggesting that the solubility enhancement was due to more ionization of AMP salts. Moisture adsorption studies indicated that shellac salts were more hygroscopic as AMP content increased. After storage at 40 °C, 75% RH, the acid value and insoluble solid of AMP salts were relatively constant even after storage of up to 180 days, suggesting that AMP should protect polymerization. The ABS_{1556}/ABS_{1716} values of the shellac salts were rapidly decreased after storage, especially for those consisting of a high percentage of AMN. Thus, AMP should bind much tighter at the carboxylate binding site as compared with AMN, resulting in more solubility and stability. In conclusion, optimized shellac properties could be easily accomplished by composite salts formation.

Keywords: Shellac; Salt; Enteric; Film; Stability; Ammonia; 2-Amino-2-methyl-1-propanol

1. Introduction

Shellac is a purified resinous secretion of lac insects, *Laccifer Lacca*, which are mostly cultivated in host trees in India and Thailand. The shellac is widely used in the food industry, to some extent still in the pharmaceutical industry and a market of growing interest in nutritional supplement, health supplement, and nutriceuticals [1]. In the pharmaceutical industry, shellac has been used for moisture protection and glossing, while the use for enteric coating of pharmaceutical products has greatly declined [2]. Severe problems associated with enteric properties are low solubility at the pH of the intestine and lesser stability of shellac as compared to synthetic and semi-synthetic enteric polymers, e.g., polyacrylates and cellulose derivatives [3]. The shellac possesses a high pK_a between 6.9 and 7.5 and begins to dissolve at pH 7.0. However, the pH in the proximal region of the small intestine is between 3.8 and 6.9 and the failure of shellac coated tablets or capsules to disintegrate at these pH media is still a major problem [2,4]. During many years, several attempts have been made to clarify the problem. Pearnchob et al. developed a faster disintegrated shellac coated capsule by adding organic acids, e.g., sorbic acid and benzoic acid. The addition of organic acids decreased the disintegration time in phosphate buffer (pH 6.8) while the behavior in 0.1 N hydrochloric acid was unchanged [5]. The hydrolysis process was also used as a method for improving the

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doi:10.1016/j.ejpb.2007.04.008

solubility of shellac. The partially hydrolyzed shellac showed greater solubility and dissolution, especially at pH 7.0 and lower [6]. However, a stabilization method for shellac is not completely developed.

As shown in Fig. 1, shellac is composed of polyesters and single esters that contain a large amount of hydroxyl and carboxylic acid. The polymerization can occur by the esterification among the functional groups and was the cause of instability [7]. Since the polymerization occurred via a carboxyl group, the protection at the carboxylic acid should be a possible means for improving the stability of shellac. Specht et al. demonstrated that application of shellac from an aqueous solution of alkali salts showed better stability than the application from ethanolic solution [8]. Similar results were observed by our group. The ammonium salt of shellac demonstrated better stability and solubility, as compared with shellac in free acid form [9]. However, the stability of ammonium salts was decreased after storage at stress condition for a long period, especially under the test condition of a tropical zone (40 °C, 75% RH) for more than 3 months. The loss of ammonium ion from the carboxylic group might be a possible explanation that still needed to be investigated. In addition, another salt forming agent, especially one more tightly bound to the carboxylic acid, should be examined and the mechanism of the stabilization process should be further clarified.

The aim of the present study was to evaluate the effect of salt forming agents on enteric properties and stability of shellac. Ammonium hydroxide (AMN), 2-amino-2-methyl-1-propanol (AMP) and the combination of both bases were selected as the salt forming agents in this study. The shellac samples, in acid form and various salt forms, were prepared and comparatively evaluated.

2. Materials and methods

2.1. Materials

Shellac was purchased from Thananchai Part., Ltd. (Bangkok, Thailand). Other reagents used were of analytical grade and used as received.

2.2. Methods

2.2.1. Preparation of partially hydrolyzed shellac

Partially hydrolyzed shellac was prepared by a previously described method [6]. Shellac (200 g) was dissolved in 2% w/w sodium hydroxide solution (1800 g) and kept at 30 ± 1 °C for 8 min. The mixtures were then immediately neutralized with 2 N sulfuric acid, washed with excess water, and dried. The partially hydrolyzed shellac was kept in the refrigerator prior to use.

2.2.2. Preparation of shellac films in acid form and various salts forms

Shellac films, in acid form and salt forms, were prepared using the casting/solvent evaporation technique. For the acid form, the partially hydrolyzed shellac was dissolved in ethanol overnight and then the final concentration was adjusted to 12% w/w. The solution was poured onto a polytetrafluoroethylene (PTFE) plate and allowed to evaporate at 50 °C for 2–3 h. The film was peeled off and stabilized at 25 °C, 75% RH prior to testing. In the case of salt forms, films of the 0:100 (100% AMN) salt, 100:0 (100% AMP) salt and 20:80, 40:60, and 80:20 AMP:AMN composite salts were prepared. The partially hydrolyzed shellac was dispersed in water, then AMN, AMP or combinations of these bases were added. The amounts of added bases were calculated in accordance with the acid value of partially hydrolyzed shellac. The solutions were stirred overnight and then the cast films were prepared by the same method as described above, except that the drying time was changed to 4–5 h.

2.2.3. Characterization of films

2.2.3.1. Film thickness. The film thickness (160 ± 30 μm) was measured at five points with a thickness gauge Mini-Test 600 (ElektroPhysik Dr. Steingroever GmbH & Co. KG, Germany).

2.2.3.2. Acid value and insoluble solid. Acid value (AV) was determined by the acid–base titration method adapted from the United States Pharmacopeia [10]. An accurately

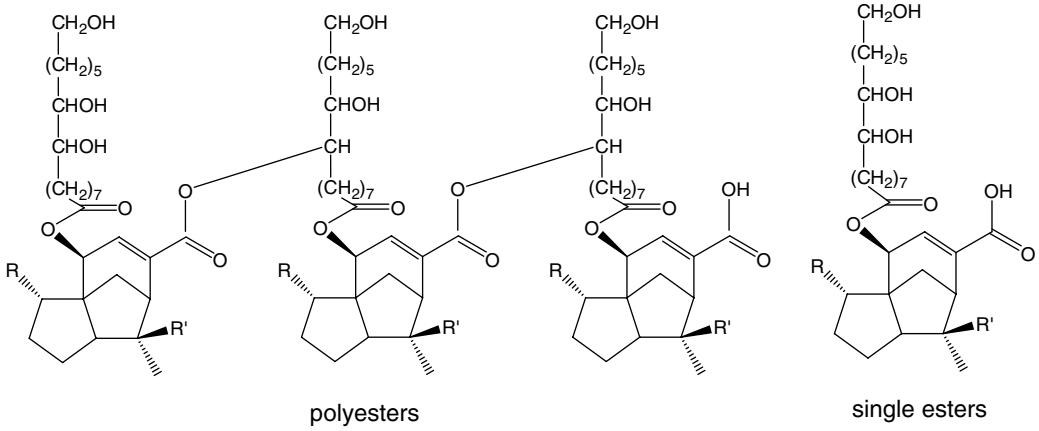

Fig. 1. Chemical structure of shellac.