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Research paper

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

Sontaya Limmatvapirat [a,*], Chutima Limmatvapirat [b], Satit Puttipipatkhachorn [c], Jurairat Nuntanid [a], Manee Luangtana-anan [a]

[a] *Department of Pharmaceutical Technology, Silpakorn University, Nakhon Pathom, Thailand*
[b] *Department of Pharmaceutical Chemistry, Silpakorn University, Nakhon Pathom, Thailand*
[c] *Department of Manufacturing Pharmacy, Mahidol University, Bangkok, Thailand*

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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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[*] Corresponding author. Department of Pharmaceutical Technology, Faculty of Pharmacy, Silpakorn University, Nakhon Pathom 73000, Thailand. Tel.: +66 34255800; fax: +66 34255801.
E-mail address: sontaya@email.pharm.su.ac.th (S. Limmatvapirat).

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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

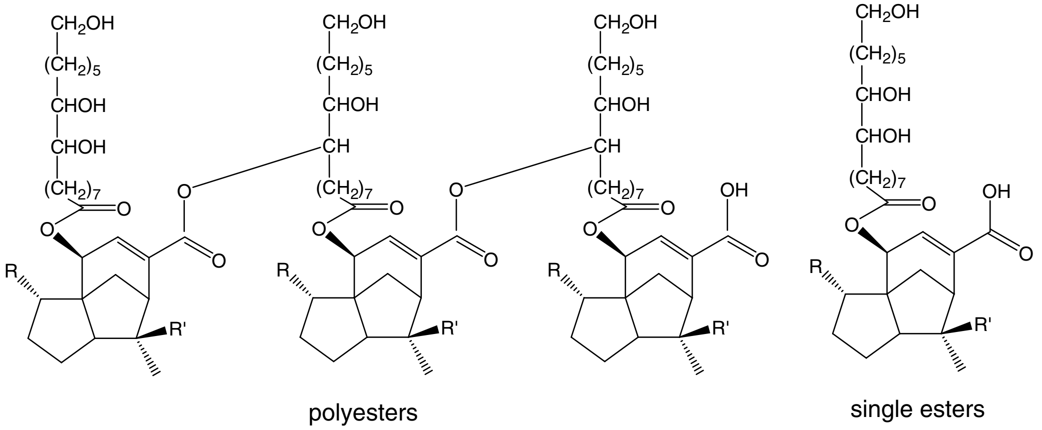

Fig. 1. Chemical structure of shellac.

weighted 3 g of finely ground shellac film was dissolved in ethanol overnight and finally adjusted to the total weight of 39 g with ethanol. The solution was centrifuged and filtered through filter paper. The 26 g of filtrate (equivalent to 2 g of shellac) was titrated with 0.1 N sodium hydroxide VS. The end point was determined by pH meter instead of using color indicator due to the dark color of shellac. The insoluble solid on filter paper was washed with excess ethanol and dried at 70 °C until the dried weight was constant, and then the percentage of insoluble solid was calculated.

2.2.3.3. Solubility. The solubility of the film was determined by a method adapted from Wu et al. [11]. At first, the film was cut in a square of 1 cm × 1 cm and weighed. The film was then placed in each of six tubes of the basket of USP disintegration apparatus which maintained the temperature at 37 ± 2 °C. The simulated gastric fluid (SGF) was used as immersion fluid for the first 2 h. After immersion in SGF, the film was transferred to buffer at various pH values for the next 3 h. The resulting film was dried at 70 °C for 12 h, and reweighed. The percentage of dissolved film was calculated from the percent weight loss of film.

In the case that the film was completely dissolved within 3 h in buffer, the dissolution times were recorded.

2.2.3.4. Moisture adsorption. Moisture adsorption was determined by placing shellac samples into a controlled humidity environment at a constant temperature until equilibrium [12]. After drying samples until constant weight, the dried samples were placed into environments of various relative humidities above salt solutions in desiccators. The relative humidities were 11% RH (lithium chloride), 32% RH (magnesium chloride), 54% RH (sodium dichromate), 75% RH (sodium chloride), 85% RH (potassium chloride), and 93% RH (potassium nitrate). The samples were equilibrated at each condition for 5–10 days at 25 ± 2 °C and then immediately weighed after removal from the desiccators. The weight gain of the samples was recorded.

2.2.3.5. Mechanical properties. The mechanical properties of the shellac films were measured by a puncture test as previously described [13]. A texture analyzer (TA.XT.plus Texture Analyzer, Stable Micro Systems, UK), equipped with a spherical puncturing probe (diameter 5 mm), was employed. The film was placed in a holder with a cylindrical hole ($r = 1.0$ cm). The probe was driven through the film with a speed of 0.1 mm/s and force–displacement curves were recorded through a 50 N load cell. The maximum load and the maximum displacement of films were measured, and then converted to puncture strength, elongation at puncture and modulus at puncture. The parameters were calculated as follows [14]

$$\text{Puncture strength} = \frac{F_{\max}}{A_{\mathrm{CS}}}$$

where $F_{\max}$ is the maximum applied force, A_{CS} the cross-sectional area of the edge of the film located in the path of the cylindrical hole of the film holder, with $A_{\mathrm{CS}} = 2r\delta$, where r is the radius of the hole and δ is the thickness of the film

$$\text{Elongation } (\%) = \frac{\sqrt{r^2 + d^2} - r}{r} \times 100$$

where r is the radius of the film exposed in the cylindrical hole of the film holder and d represents the displacement of the probe from the point of contact to point of puncture.

$$\text{Modulus at puncture} = \frac{\text{Puncture strength}}{\text{Elongation } (\%)}$$

2.2.3.6. Differential scanning calorimetry (DSC). Films of shellac samples were dried over silica gel and pulverized with agate mortar. DSC curves of ground samples were recorded using a differential scanning calorimeter (Sapphire, Perkin Elmer, USA). Each sample (5–6 mg) was accurately weighed into an aluminum pan. The measurements were performed between 10 and 250 °C at a heating rate of 10 °C/min. To determine the effect of pulverization, shellac samples were also directly casted into DSC pans and measured by the same condition.

2.2.3.7. Hot stage microscopy (HSM). All HSM photographs were recorded using a light microscope (Olympus, BX50, Japan) equipped with hot stage controller (Collet, S516P, Japan). Finely ground shellac films were observed under the microscope at a heating rate of 10 °C/min. Changes in the morphology of various salts were comparatively evaluated as a function of temperature.

2.2.3.8. Fourier transformed infrared (FTIR) spectroscopy. FTIR spectra of samples were recorded with a FTIR spectrophotometer (Nicolet, Magna 750, USA) using the KBr disc method. Each film was pulverized, gently triturated with KBr powder and then pressed using a hydraulic press at a pressure of 5 tons. The KBr disc was placed in the sample holder and scanned from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

2.2.4. Stability study

The stability study was carried out under stress conditions of tropical areas. Shellac films were kept in a stability cabinet at 40 °C, 75% RH for 6 months. The films were periodically withdrawn and then characterized by the methods described above.

2.2.5. Statistical analysis

Data were expressed as means ± standard deviation (SD). The statistical analysis was carried out using analysis of variance (ANOVA) at the 0.01 significance level.

3. Results and discussion

3.1. Physicochemical properties

The effects of salt forming agents (bases) on physicochemical properties, including solubility, acid value and insoluble solid, were determined. Shellac salts with various ratios of AMP:AMN at 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0 were compared with the free acid form.

Fig. 2 demonstrates the percentage dissolved (bar chart) and dissolving time (line chart) of various shellac forms after immersion in simulated gastric fluid for 2 h and transferring to buffer at various pH values for 3 h. From our previous work [6], the pH solubility profile of shellac was established. The results demonstrated that shellac was partially dissolved at pH 7.0 and completely dissolved at pH 7.3 and higher. Therefore, we selected pH 7.0 and pH 7.3 as representative pH values for the study of percentage dissolved and dissolving time, respectively. The percentage dissolved of shellac salts was significantly increased while the dissolving time was significantly decreased ($p < 0.01$), suggesting the enhancement of aqueous solubility after salt formation. In addition, the percentage dissolved was with increase of the AMP fraction, i.e., percentage dissolved of 100:0 > 80:20 > 60:40 > 40:60 > 20:80 > 0:100 AMP:AMN. The dissolving time was also decreased with increasing AMP content. Therefore, AMP salt not only increased the percentage of dissolved shellac at lower pH but also increased the rate of dissolution at higher pH. The result suggested that AMP should be a more suitable salt forming agent for enhancing aqueous solubility as compared to AMN.

The total number of carboxyl groups, expressed by acid value, controls the solubility of enteric polymers. In addition, the ionization also affects the aqueous solubility. As pH increases, the acid–salt equilibrium shifts to the formation of the ionized form with increasing aqueous solubility. Thus, the solubility of shellac is assumed to be controlled by 2 parameters, i.e., the total number of carboxyl groups and the carboxylate/carboxylic acid ratio.

The acid value of shellac was increased as propagation of alkaline hydrolysis time. The increment of solubility was observed in partially hydrolyzed shellac [6]. To study the extent of hydrolysis during film preparation by various bases, the acid value of each salt form was determined. Acid values of acid form, 0:100, 20:80, 40:60, 60:40, 80:20, and 100:0 AMP:AMN salts were 90, 97, 90, 92, 91, 90, and 90, respectively. The acid values of all salt forms were not increased as compared with the acid form. The result suggested that alkaline hydrolysis did not obviously occur during film preparation with both bases. Therefore, the improvement of aqueous solubility was not due to the increment of total number of carboxyl groups and should involve the increase of the carboxylate/carboxylic acid ratio.

3.2. FTIR spectroscopy

FTIR spectroscopy was employed for monitoring the conversion of carboxylic acid to carboxylate. Fig. 3 illustrates the FTIR spectra of shellac in acid form and various salt forms. The acid form showed a broad band peak in the range of 3600–3200 cm^{-1} with the maxima around 3400 cm^{-1}, which could be attributed as O—H stretching. The peak at 1716 cm^{-1} due to C═O stretching of the carboxylic acid (and also overlapped by that of an aldehyde or ketone) was also observed. The 0:100 AMP:AMN salt showed the new peaks at 1556 and 1385 cm^{-1} which were assigned as asymmetric and symmetric C═O stretching of carboxylate, respectively, while the relative absorbance of the peak at 1716 cm^{-1} declined. The results suggested the conversion of carboxylic acid to carboxylate after salt formation. The 100:0 AMP:AMN salt showed similar results and demonstrated the more pronounced effect on carboxylate formation. The relative absorbance ratios of the FTIR peaks assigned to C═O stretching of carboxylate and carboxylic acid ($\text{ABS}_{1556}/\text{ABS}_{1716}$) were increased with an increase of the AMP fraction (100:0 > 80:20 > 60:40 > 40:60 > 20:80 > 0:100 AMP:AMN). Thus, it was confirmed that higher solubility of AMP salts was due to the increased ionization of shellac.

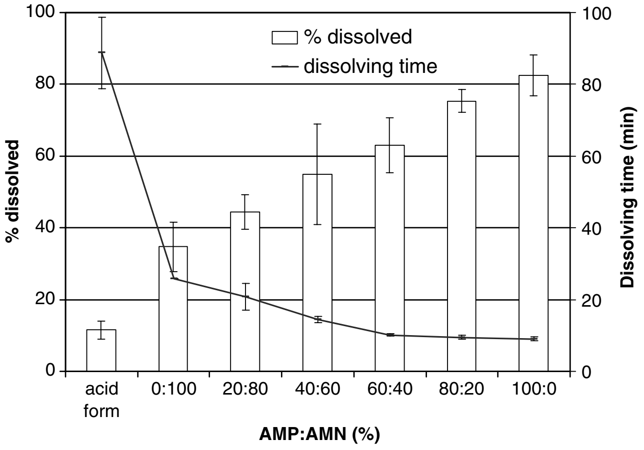

Fig. 2. Effect of salt formation on percentage dissolved at pH 7.0 and dissolving time at pH 7.3 of shellac films.

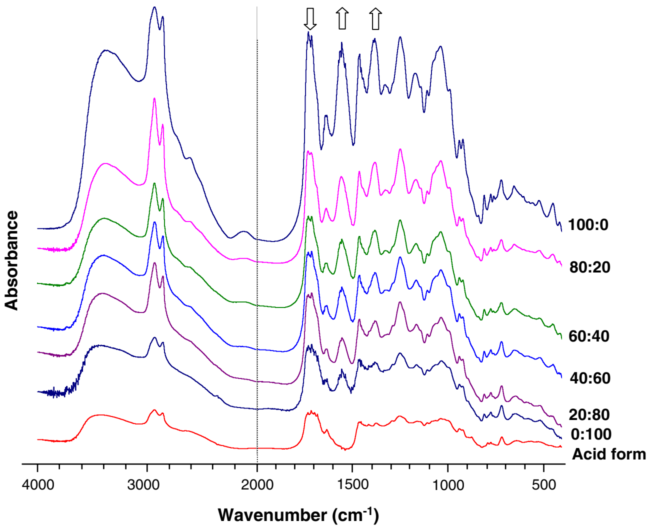

Fig. 3. FTIR spectra of acid form and various salt forms (AMP:AMN) of shellac.

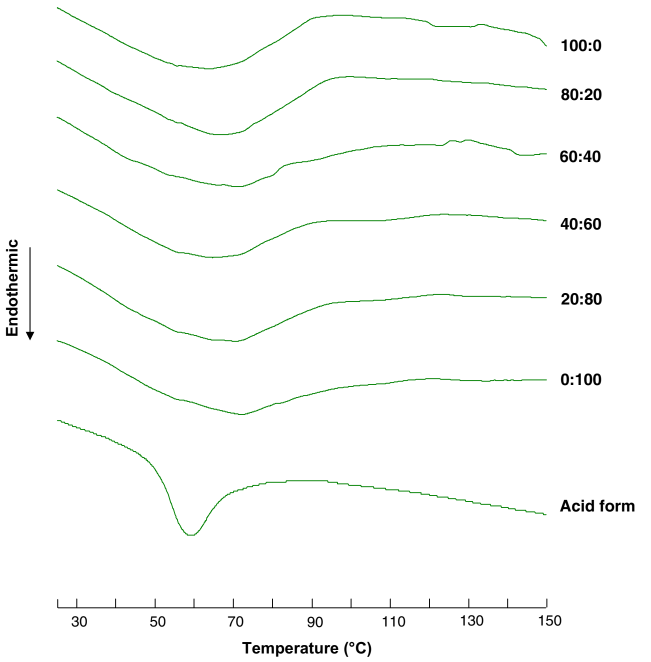

Fig. 4. DSC curves of acid form and various salt forms (AMP:AMN) of shellac.

Generally, ionization of acid depended on the basicity of used bases. The pK_a values of AMP and AMN were 9.69 and 9.25, respectively [15]. The more basic AMP base should be a possible explanation for the increased ionization of shellac. However, the pK_a value of AMP was slightly higher than that of AMN, thus other factors might also affect the solubility of shellac salts. The AMP^+ ion might interact more strongly at the COO^- binding site, as compared with NH_4^+. The detail of interaction will be further discussed in the section on stability study.

3.3. Thermal analysis

To investigate the correlation between melting point and solubility and also to further characterize shellac salts, thermal analysis was performed. Fig. 4 shows DSC curves of shellac in acid form and various salt forms. The acid form indicated a clear endothermic peak at 58 °C, while the corresponding salt forms demonstrated a broad endothermic region in the range of 20–130 °C. The broad endothermic region tended to shift to the lower temperature with increasing percentage of AMP.

To clarify the unclear thermal behavior on DSC curves, we employed hot stage microscopy (HSM) for the study. The HSM photomicrograph of the acid form revealed that the endothermic peak of the acid form was due to melting, as shown by the liquid droplet formation after heating to 60 °C. The 0:100 AMP:AMN salt did not clearly show the fusion. The only partial melt at the surface was observed with even heating to more than 100 °C. The broad endothermic region in the DSC curve should be due to water loss and partial melting (the moisture content of shellac salts was about 5–6% w/w). The endothermic band due to loss of water should obscure the peak, assigned to melting. Similar results were observed for the 20:80 AMP:AMN salt. The incomplete fusion, though more obviously seen, was detected. However, the complete fusion was observed in 40:60, 60:40, 80:20, and 100:0 AMP:AMN salts. The samples were entirely melted at 135, 115, 105, and 90 °C, respectively. The results suggested that the melting temperature decreased as the percentage of AMP increased. The results also agreed with the work of O'Conner and Corrigan. The study indicated the inverse relationship between melting point and solubility [16]. Thus, the lower melting point of AMP salt should correlate with the higher solubility as compared with the AMN salt.

3.4. Moisture adsorption study

Hygroscopicity is also an important parameter for selection of a suitable salt form. Although the shellac possessed very low water vapor permeability as compared with other enteric polymers [3], the salt formation might affect the hygroscopicity. To study the effect of salt forming agents on hygroscopicity, moisture adsorption of the acid form and various salt forms of shellac was elucidated (Fig. 5). The acid form showed significantly lower moisture adsorption as compared with the salt forms ($p < 0.01$). Moisture uptake of the acid form was less than 3%, even when increased to 93% RH while that of 100:0 AMP:AMN salt was more than 20%. The higher fraction of AMP salts showed tendency to absorb more moisture, especially after storage above 75% RH. Since the hygroscopicity of salts was dependent on their aqueous solubility [17], the increased solubility of the AMP salt should be a possible explanation for more water adsorption as compared with that of the AMN salt. In addition, a high fraction of AMP should be avoided regarding hygroscopic concern.

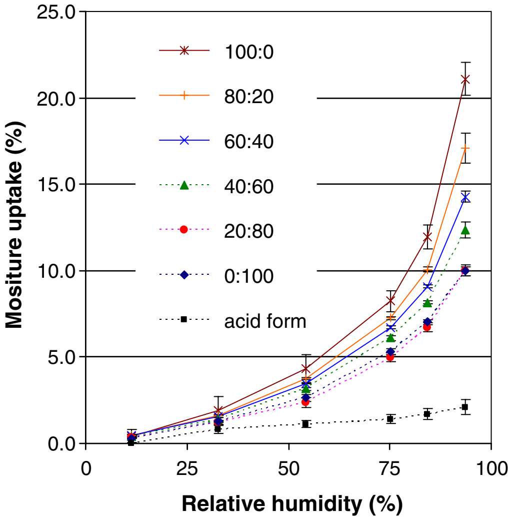

Fig. 5. Moisture adsorption of acid form and various salt forms (AMP:AMN) of shellac.

3.5. Mechanical properties

Mechanical properties of shellac, including puncture strength, elongation, and modulus at puncture, are shown in Fig. 6. The change of shellac from the acid form to 0:100 AMP:AMN salt significantly increased ($p < 0.01$) the modulus of film (Fig. 6a). The high modulus resulted from the high puncture strength and the low percentage of elongation of 0:100 AMP:AMN (Fig. 6b). The data suggested the hardness and brittleness of the film after ammonium salt formation. A similar change of mechanical properties was observed by using other enteric polymers, including cellulose acetate phthalate, cellulose acetate trimellitate and hydroxypropyl methylcellulose phthalate. Ammoniated enteric films showed somewhat more brittleness than the acid form prepared from organic solvent [18].

The flexibility of films was increased when the percentage of AMP salt was increased, as observed by the increment of percentage of elongation. The percentage of elongation was increased 12 times after changing the ratio of AMP:AMN from 0:100 to 100:0. From the point of flexibility, AMP salts should be more suitable for film formation than AMN salts. However, the puncture strength, which indicated the resistance to mechanical force during coating, had a tendency to decline. The puncture strengths of 20:80, 40:60, 60:40, 80:20, and 100:0 AMP:AMN salts were 9.8, 8.3, 6.6, 3.2, and 2.4 MPa, respectively. Therefore, composite salts, especially in the ratio of AMP:AMN from 20:80 to 60:40, should be more suitable than pure ammonium or AMP salts, regarding the optimized strength and strain of the film.

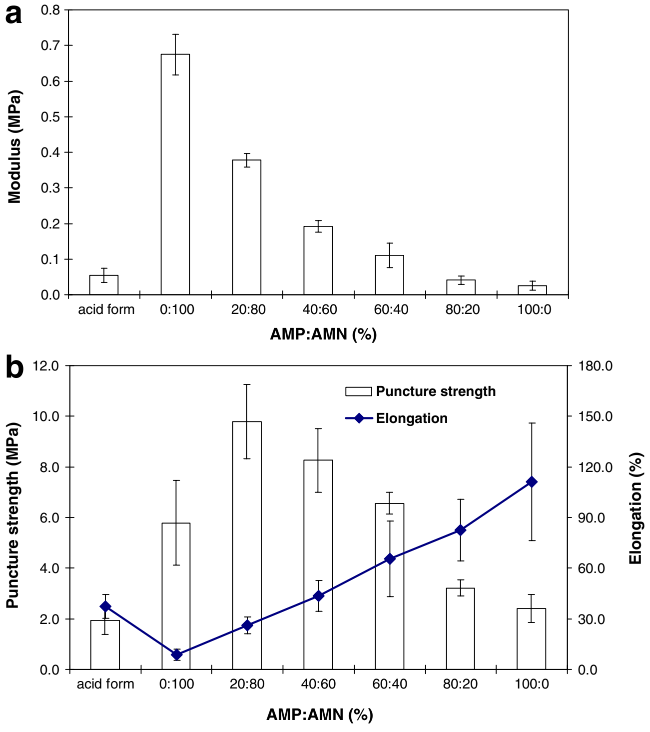

Fig. 6. Mechanical properties of acid form and various salt forms (AMP:AMN) of shellac: (a) modulus at puncture, (b) puncture strength and percentage of elongation.

Generally, the addition of plasticizers increases percentage of elongation, but often is accompanied by the reduction of strength and modulus. Various plasticizers, including triethyl citrate and polyethylene glycol, could decrease the glass transition point and change the mechanical properties of shellac film [5,19]. However, the causes of modified mechanical properties of shellac salts were considered to be different, as plasticizer free films were prepared. With regard to the moisture adsorption study in Fig. 5, the moisture content was increased with increasing percentage of AMP. Therefore, it should be possible that water could act as a plasticizer, resulting in more change of mechanical properties of AMP salts. Similar plasticization effects of water have been recognized [20]. Another possibility should relate to the interaction between salt forming agent and polymer chain of shellac. Since AMP possessed an extra hydroxyl group as comparing with AMN, the hydrogen bond might promote the interaction between AMP and the polymer chain, resulting in more plasticization effect. The more plasticization effect agreed with the lower melting temperature as increasing percentage of AMP.

3.6. Stability study

3.6.1. Effect of ageing on insoluble solid

Insoluble solid is one of the parameters that indicate the stability of shellac. After storage, shellac was polymerized to form an insoluble solid which could not dissolve in ethanol. Fig. 7 demonstrates the percentage of insoluble solid of shellac in the acid form and various salt forms after storage. As expected, the percentage of insoluble solid of acid form was immediately increased as

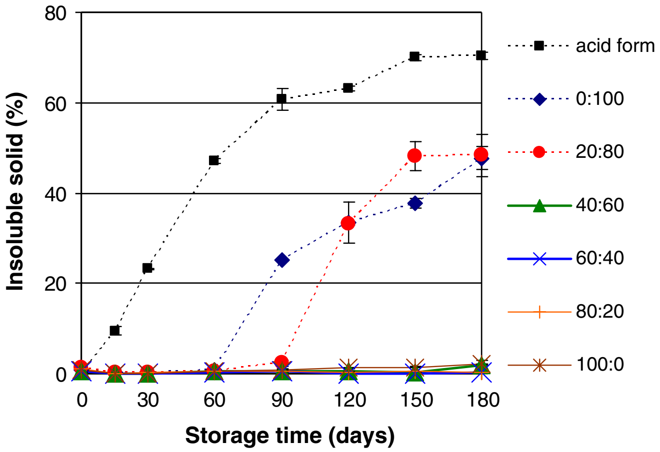

Fig. 7. Change of percentage of insoluble solid of acid form and various salt forms of shellac after storage at 40 °C, 75% RH for 6 months.

prolongation of storage time. The pronounced increment of percentage of insoluble solid was observed after storage for 15 days ($p < 0.01$). However, the percentage of insoluble solid of 0:100, 20:80, and 40:60 AMP:AMN salts was increased after storage for 60, 90 and 180 days, respectively. The 60:40, 80:20, and 100:0 AMP:AMN salts did not show a clear increment of percentage of insoluble solid, even with storage of up to 6 months. These results indicated that the polymerization was protected due to salt formation, and the more stabilization effect of AMP salts over AMN salts was observed.

3.6.2. Effect of ageing on percentage dissolved of shellac films at pH 7.0

We also studied the stability of shellac films by monitoring the change of percentage dissolved at pH 7.0 (Fig. 8). For 60:40, 80:20, and 100:0 AMP:AMN salts, the percentage of dissolved films was not changed with increasing storage time. The result agreed well with the percentage of insoluble solid, confirming that polymerization did not occur even with storage of up to 6 months. The percentage dissolved of 40:60 AMP:AMN salt was rapidly decreased at the initial period and slightly decreased after 30 days. Since the percentage of insoluble solid was not significantly changed (Fig. 7), the decrease of percentage dissolved of 40:60 AMP:AMN salt should not be involved with the polymerization. The conversion of carboxylate form to carboxylic acid after losing some AMN or AMP from the carboxylate binding site could be a possible reason for reduction of the percentage dissolved. For 0:100 or 20:100 AMP:AMN salts, the percentage dissolved was significantly decreased as increasing storage time ($p < 0.01$). Both carboxylate conversion and polymerization should be possible explanations for the result. The conversion of carboxylate to carboxylic acid should be a reason for decreasing of percentage dissolved at the initial period. After carboxylate conversion, the polymerization could then initiate, resulting in greater decrease of percentage of dissolved films after prolonged storage.

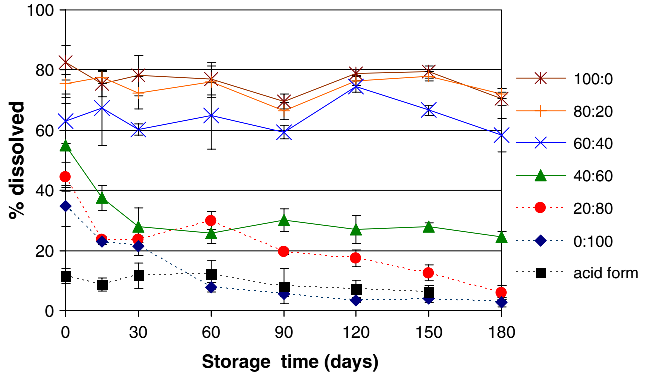

Fig. 8. Change of percentage dissolved at pH 7.0 of acid form and various salt forms of shellac after storage at 40 °C, 75% RH for 6 months.

3.6.3. Investigation of ageing mechanism by FTIR spectroscopy

In order to investigate the increased stabilization effect of AMP over AMN, the FTIR spectra of all shellac salts were comparatively evaluated for 6 months. The changes of ABS_{1556}/ABS_{1716} (which represented the carboxylate/carboxylic acid ratio as discussed in Section 3.2) of all shellac salts are illustrated in Fig. 9. For 0:100 AMP:AMN salt, the absorbance ratio was rapidly decreased after storage, however, for the 100:0 AMP:AMN salt, the absorbance ratio was gradually decreased. After storage for 6 months, the absorbance ratio of 100:0 AMP:AMN salt was 7 times more than the 0:100 AMP:AMN salt. In addition, the slower decrease of the absorbance ratio was observed with increasing the AMP fraction. The results suggested that AMP should interact much stronger than AMN at the carboxylate binding site, and prevent the conversion of carboxylate to carboxylic acid.

Fig. 10 demonstrates the proposed diagram of salt formation and ageing mechanism of various forms of shellac. The acid form was rapidly polymerized by esterification among hydroxyl and carboxyl groups of polymer chains of shellac after ageing, resulting in increasing of the percentage of insoluble solid and lowering of the acid value and aqueous solubility. However, the polymerization could be protected by salt formation with AMN or AMP. The carboxylic acid to carboxylate conversion could increase the solubility and stabilize the shellac. AMP should more strongly interact with the carboxylate, resulting in more ionization, plasticization and stability as compared to AMN. The increased interaction was assumed to involve the hydrogen bond formation between hydroxyl groups of AMP and shellac. In addition, the steric effect of the large molecular size of AMP might cause the polymer chains to separate from each other and reduce the possibility of esterification among polymer chains of shellac.

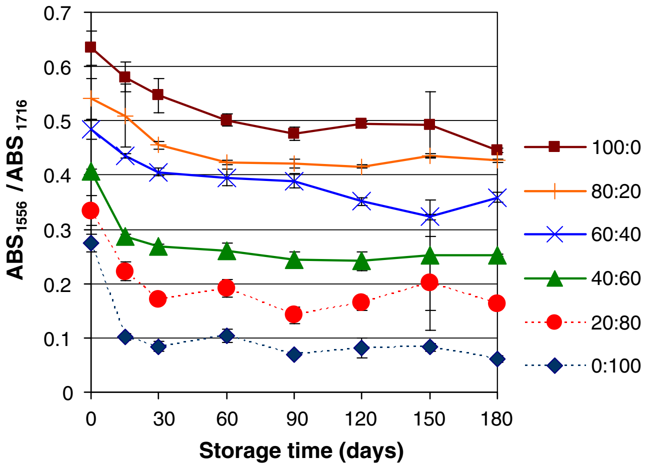

Fig. 9. Change of ABS_{1556}/ABS_{1716} of various salt forms after storage at 40 °C, 75% RH for 6 months.

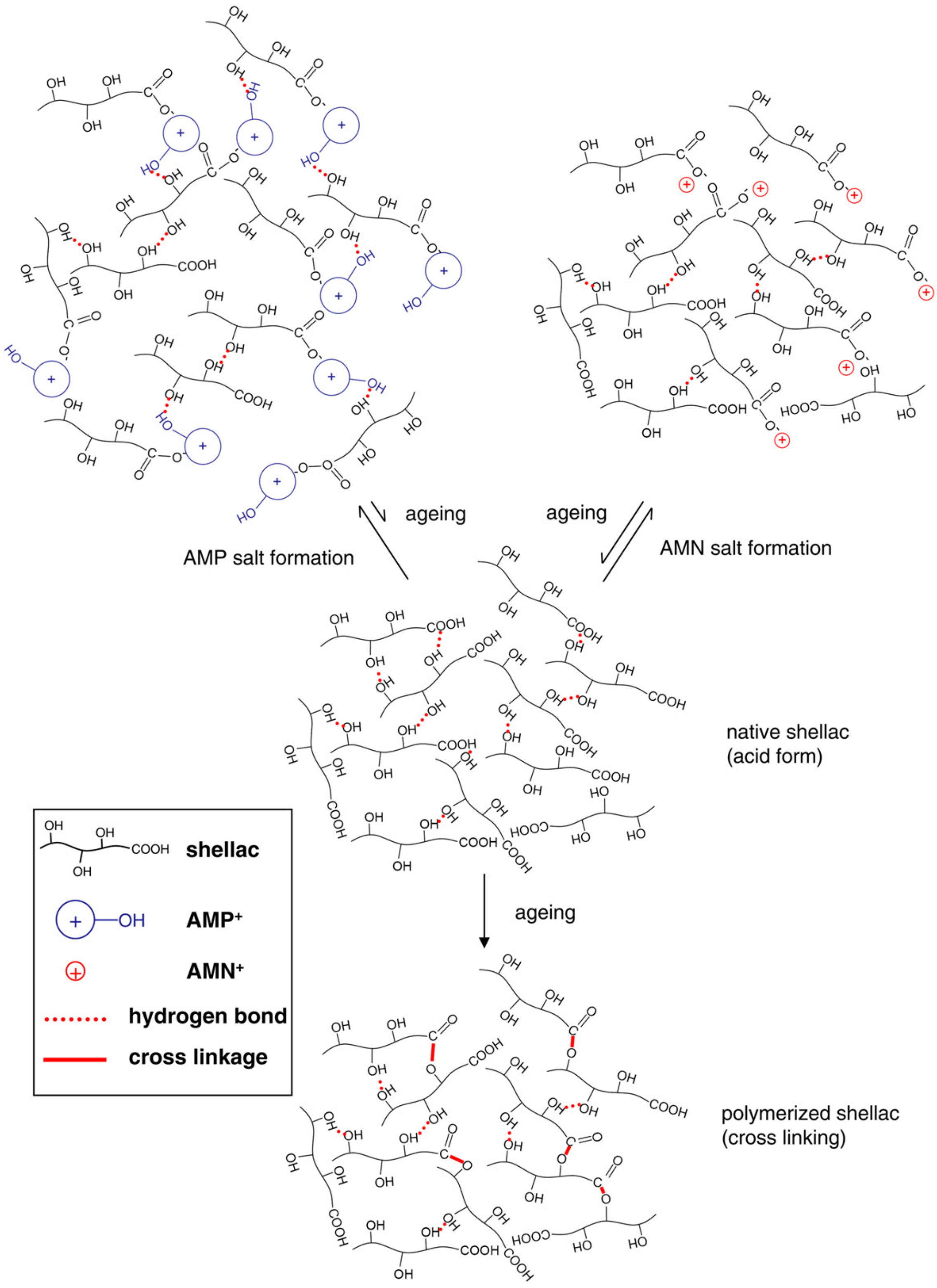

Fig. 10. Proposed diagram of salt formation and ageing of various forms of shellac.

4. Conclusion

The improved enteric properties of the shellac films were easily achieved by AMP:AMN composite salts formation. The main disadvantages of AMN salt, including less solubility and less stability, were compensated for by combination with AMP salt, whereas the main disadvantages of AMP, including high hygroscopicity and low film strength, were counterbalanced by combination with AMN salt. The optimum ratio of AMP:AMN should be in the range of

40:60–80:20 with regard to solubility, hygroscopicity, mechanical properties and stability of film.

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