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Research paper

Formation of shellac succinate having improved enteric film properties through dry media reaction

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Abstract

The aim of this study was to improve enteric properties of shellac by the formation of succinate derivative through dry media reaction. Shellac and succinic anhydride were mixed and then co-ground by planetary ball mill. The ground mixture was then activated by heating for various times and washed for removal of excess succinic anhydride. The ground mixtures and the heat-activated mixtures were characterized by physical and chemical tests, including acid value, FTIR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, thermal analysis and film properties. The results demonstrated that acid values of heat-activated shellac mixtures increased with the increase of annealing time, suggesting the presence of carboxylic acid moieties of succinate at shellac molecules. The results were in good agreement with the DSC thermograms. The melting peak of shellac disappeared after heating, while melting peak of succinic anhydride gradually decreased, suggesting the utilization of succinic anhydride for the esterification. The shellac succinate formation was also confirmed by ^{1}H NMR and ^{13}C NMR spectroscopies. Film prepared from shellac succinate showed improved solubility, especially at the pH of small intestine (5.8–6.7), as compared to native shellac. The shellac succinate film also demonstrated better mechanical property, in terms of increased flexibility. In conclusion, solid-state formation of shellac succinate ester, which had improved enteric properties, was easily accomplished under the concept of "green approach".

Keywords: Shellac; Shellac succinate; Enteric polymer; Co-grinding; Mechanochemistry

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1. Introduction

Shellac is a purified resin derived from lac insects which are mostly grown in host trees in China, India and Thailand. Due to some interesting properties, including low water permeability, low acid permeability, gloss and natural origin, shellac has been used for pharmaceutical, agriculture, confectionary and food products. For pharmaceutical application, shellac is used for sealing, enteric coating and controlled drug delivery [1–4]. However, the utilization of shellac, especially in pharmaceutical industry, has greatly declined because of low solubility at intestinal pH, instability and the replacement by synthetic polymers [5].

As shown in Fig. 1, shellac molecules consist of hydroxyl and carboxyl groups. The low number of carboxylic acid per shellac molecule and the high pK_a of carboxylic acid lead to the low solubility [6–8]. Additionally, the polymerization can occur by the esterification among the functional groups in shellac molecules which is the cause of instability [9]. Therefore, several attempts have been made to modify the

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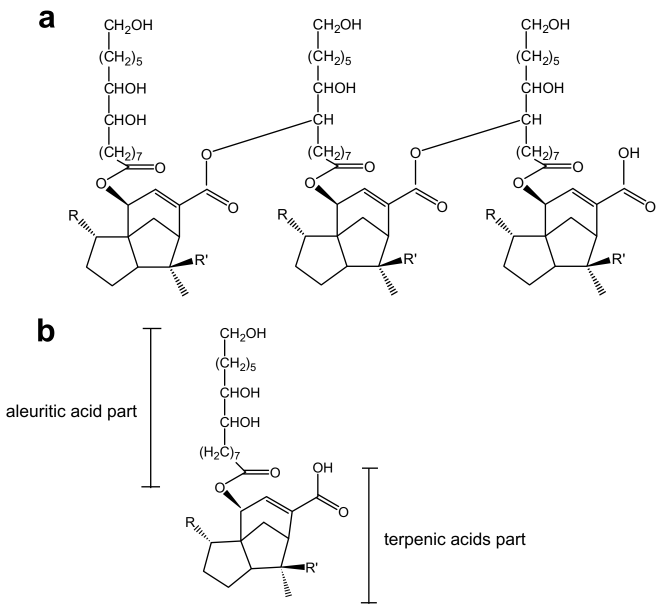

Fig. 1. Chemical structure of shellac: polyesters (a), single esters (b).

structure of shellac. The hydrolysis process was employed as a simple method for improving the solubility of shellac. The partially hydrolyzed shellac, having more carboxylic acid groups, showed greater solubility and dissolution, especially at pH 7.0 [10]. However, the stability problems were not solved since the polymerization still occurred [11]. The salt formation was proposed to inhibit polymerization by protection at the carboxylic acid group. The ammonium salt of shellac demonstrated better stability, as compared to shellac in acid form [11,12]. Recently, we also introduced the novel salt of 2-amino-2-methyl-1-propanol (AMP) which demonstrated better solubility and stability as compared to ammonium salt [13,14]. Nevertheless, the structure modification of shellac has been only focused on carboxylic acid while modification of hydroxyl group has not been reported. Kokubo et al. developed the cellulose-derived polymer that dissolved at low pH by esterification of the hydroxyl group with cyclic anhydrides. The dissolving pH of the polymer can be controlled in the range from pH 3.5 to 4.5 by varying the content of acid groups on the base polymer [15]. Since shellac consists of several hydroxyl groups as illustrated in Fig. 1, esterification with cyclic anhydride, e.g. succinic anhydride, should be a possible mean for increasing the number of carboxyl groups.

A dry media reaction or solid-state reaction is a chemical reaction system in the absence of solvent. Avoiding organic solvents during the reactions lead to a safe, clean, efficient, and economical technology [16]. Mechanochemical process can be applied in the field of dry media reaction. The process is involved in grinding of materials with, or without thermal activation. It was proved to be an efficient methodology for inducing solid-state transformation, including amorphization [17], complexation [18,19], and synthesis [20]. However, the application of mechanochemistry for the syntheses of shellac derivatives was not yet investigated.

The purpose of this study was to investigate the possibility of dry media reaction for the synthesis of shellac succinate. Shellac and succinic anhydride were co-ground and activated by heating. The shellac samples were evaluated by instrumental analysis. In addition, the film of shellac and shellac succinate was prepared and comparatively evaluated.

2. Materials and methods

2.1. Materials

Shellac (SHL) was purchased from Thananchai Part., Ltd. (Bangkok, Thailand). Succinic anhydride (SUC) was obtained from Merck (Darmstadt, Germany). All other chemicals were of analytical grade.

2.2. Methods

2.2.1. Preparation of shellac:succinic anhydride ground mixture

At first, the physical mixture of SHL and SUC was prepared. The SHL (115.7 g) and succinic anhydride (84.3 g) were mixed in a plastic bag for 5 min. The physical mixture was transferred to a 500 ml stainless steel grinding bowl together with 5 stainless steel grinding balls having a radius of 30 mm and then ground by planetary ball mill (PM 100, Retsch, Germany). The grinding speed was set to 400 rpm. To avoid excessive heat, the mill was stopped every 5 min and the grinding bowl was soaked in ice bath before the next grinding cycle. The total grinding time, excluding soaking time, was fixed to 90 min. The ground mixture was thoroughly removed and then stored in a freezer before use.

2.2.2. Preparation of shellac:succinic anhydride annealed mixture

To facilitate esterification (succinate formation), the ground mixture was then annealed at 60 °C for various times. After annealing at a predetermined period, the mixture was withdrawn and immediately washed with purified water to remove excess succinic anhydride. Some parts of annealed mixtures (without washing) were also collected for characterization. The annealed mixtures were then kept in a freezer prior to comparative characterization.

2.2.3. Characterization of shellac samples

2.2.3.1. Acid value and insoluble solid. Acid value (AV) of shellac samples was determined by the acid–base titration adapted from the United States Pharmacopeia (USP 29) [21]. An accurately weighed 3 g of shellac sample was dissolved in 95% w/w ethanol overnight and finally adjusted to the total weight of 39 g with 95% w/w ethanol. The solution was centrifuged and filtered through Whatman filter paper (an average pore size of 11 μm). The 26 g of filtrate (equivalent to 2 g of shellac) was titrated with 0.1 N sodium hydroxide VS. The equivalent point was determined by pH meter instead of color indicator due to the dark color of shellac. The insoluble solid on filter paper was washed with excess 95% w/w ethanol and dried at 70 °C until the weight was constant, and then the percentage of insoluble solid was calculated. The measurement was run in duplicate.

2.2.3.2. Differential scanning calorimetry (DSC). DSC curves of shellac samples were recorded by a differential scanning calorimeter (Sapphire, Perkin-Elmer, Japan). Each sample (5–6 mg) was accurately weighed into an aluminum pan with cover and then the pan was crimped by sample sealer. The measurements were performed between 25 and 200 °C under nitrogen gas purge at a heating rate of 10 °C/min.

2.2.3.3. Fourier transformed infrared (FTIR) spectroscopy. FTIR spectra of shellac samples were recorded with an FTIR spectrophotometer (Nicolet 4700, Thermo Electron Corporation, USA) using the KBr disc method. Each sample was dried over silica gel and pulverized. The ground sample was gently triturated with KBr powder and then made it to a disc with 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}.

2.2.3.4. NMR spectroscopy. Each shellac sample was dissolved in methanol-d_4 to obtain clear solution. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (Ettlingen, Germany), using residual solvent peaks at δ_H 4.84 and at δ_C 49.05 ppm as chemical shift reference signals. The chemical shifts were given in δ (ppm).

2.2.4. Preparation of shellac films

Shellac films were prepared using a casting/solvent evaporation technique as previously described [10]. Each shellac sample was dispersed in water and then ammonium hydroxide was added. The amount of added ammonium hydroxide was calculated in accordance with the acid value of each shellac sample. The mixture was stirred until the shellac sample was completely dissolved and kept stirring overnight. The final concentration was adjusted to 6% w/w with water. The solution was poured onto a glass plate, whose surface was treated with Aquasil®, and allowed to evaporate at 50 °C for 4–5 h. The film was peeled off and stabilized at 25 °C, 75% RH prior to testing.

2.2.5. Characterization of films

2.2.5.1. Film thickness. The film thickness (140 ± 20 μm) was measured at five points with a thickness gauge Mini-Test 600 (ElektroPhysik Dr. Steingroever GmbH & Co. KG, Germany).

2.2.5.2. Water vapor permeability of film. An adapted permeation cell for water vapor permeation (WVP) study was used according to the method described [10]. The cell consisted of a glass bottle, filled with dried granular calcium chloride, and a cap with an opened circular hole of 3–4 cm in diameter. The prepared film was placed inside the cap and then sealed tightly. The cell was then kept in a cabinet at 40 °C, 75% RH. The weight change was recorded periodically. The WVP coefficient of at least 3 cells for all films was then calculated using the following equation. WVP coefficient $= (W \times t)/(A \times \Delta P)$, where W is the amount of water permeated through the film in g/h, t is the thickness of film (m), A is the area of the exposed film (m^2), and ΔP was the vapor pressure difference (Pa). The unit of WVP is $\text{g} \times \text{h}^{-1} \times \text{m}^{-1} \times \text{Pa}^{-1}$.

2.2.5.3. Mechanical properties of film. The mechanical properties of the shellac films were measured by a puncture test as previously described [22]. 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 (radius = 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 of at least from 5 determinations were then calculated using the following equation [23]:

$$\text{Puncture strength} = \frac{F_{\max}}{A_{\text{cs}}},$$

$F_{\max}$ is the maximum applied force (N), 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 $A_{\text{CS}} = 2r\delta$, where r is the radius of the hole and δ is the thickness of the film (mm). The unit of puncture strength was MPa.

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

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

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

The unit of modulus at puncture is MPa.

2.2.5.4. pH solubility profiles. The solubility of the film was determined by a method adapted from Wu et al. [24]. At first, the film was cut in a square of 1 cm × 1 cm and weighed. The film was then placed in each of the 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 the buffer solutions 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 case the film was completely dissolved within 3 h in buffer solutions, the dissolving times were recorded.

2.2.6. Statistical analysis

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

3. Results and discussion

3.1. Formation of shellac succinate

As illustrated in Fig. 1, hydroxyl groups were observed in the structure of shellac, especially at the aleuritic acid part. The modification at the hydroxyl groups by esterification with succinic anhydride could be a possible mean for increasing the number of carboxyl groups in shellac molecules. In the study, the ground mixtures between shellac and succinic anhydride were prepared and then annealed at 60 °C from 1 to 24 h. The annealed mixtures were evaluated for succinate formation by acid value determination and various instrumental analyses.

3.1.1. Acid value and percentage of insoluble solid

Fig. 2 demonstrated the effect of heating time on acid value of annealed mixtures. The acid value was gradually increased as prolonged annealing time and the value reached the plateau after heat treatment for 9 h. The acid value of the 24-h annealed mixture was increased about 2 times as compared to that of native shellac. Since the acid value expressed the number of carboxyl groups per molecule, the increment of acid value suggested the substitution of carboxyl moieties of succinate at the side chain of shellac molecules. The formation of succinate derivative of some natural polymers, e.g., starch [25], chitosan [26], and hemicellulose from bagasse [27] was also reported. However, the reported syntheses still required organic solvent as a medium for reaction.

Insoluble solid is one of the parameters that indicate the stability of shellac. During storage, shellac was self-polymerized to form an insoluble solid which could not be dissolved in ethanol. Since shellac was subjected to heating during annealing process, so we also determined the insoluble solid for monitoring the stability of the annealed mixtures. The result demonstrated that the polymerization did not occur as indicated by less than 1.0 percent of insoluble solid even annealing up to 24 h (data not shown).

3.1.2. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to study the thermal behavior of samples and to confirm the succinate formation. Fig. 3 illustrates DSC curves of native shellac (SHL), succinic anhydride (SUC), physical mixture (SHL–SUC PM), 1-h, 6-h and 24-h annealed mixtures (SHL–SUC AM). SHL and SUC showed the endothermic peaks due to melting at 58 °C and 121 °C, respectively. The SHL–SUC PM showed two endothermic peaks at 54 °C and 116 °C which were considered to be due to the melting of SHL and SUC, respectively. With increase of annealing time, the endothermic peak of SHL gradually disappeared, while the enthalpy of endothermic peak of SUC decreased. The result indicated that SUC was utilized for the reaction during annealing process.

3.1.3. FTIR spectroscopy

In order to investigate the esterification of SHL by SUC, FTIR spectroscopy was also employed. Fig. 4 shows FTIR spectra of SHL–SUC systems. SHL showed broad O–H stretching vibration band around 3400 cm^{-1}, carbonyl stretching vibration band at 1716 cm^{-1} and C–O stretching band at 1255 cm^{-1} (as indicated by the triangle symbol) [13,28]. SUC demonstrated the two characteristic peaks at 1863 and 1784 cm^{-1} which were due to the asymmetric and symmetric carbonyl stretchings, respectively [29]. The peak at 919 cm^{-1} which was assigned to C–O stretching was also observed (as indicated by circular symbol).

The FTIR spectrum of the SHL–SUC PM was the superimposition of spectral patterns of SHL and SUC (Fig. 4c). After annealing, the relative peak intensity of SUC significantly decreased (as exemplified by the peaks at 1863 and 1784 cm^{-1}) although the peaks corresponding to SUC were still observed in the FTIR of SHL–SUC 24 h AM (Fig. 4d). The result confirmed the substitution of SUC in the reaction. In addition, the new peaks (as illustrated by star symbol) were observed. The new peaks were more clearly seen after removal of excess SUC by washing (Fig. 4e). As compared to the FTIR pattern of SHL, SHL–SUC AM demonstrated the different O–H stretching band in the range of 3000– 3400 cm^{-1}, suggesting the appearance of O–H group of the attached succinate moiety. The result was supported by the new peak at 1166 cm^{-1} which was assumed as C–O stretching of the ester linkage. In addition,

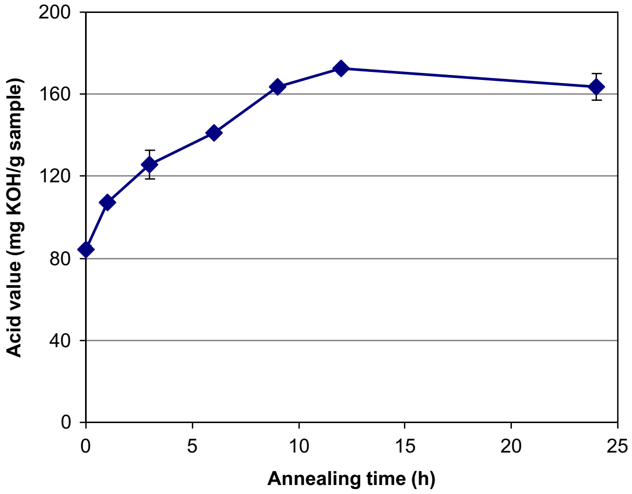

Fig. 2. Change of acid value of SHL–SUC GM after annealing at 60 °C for various times.

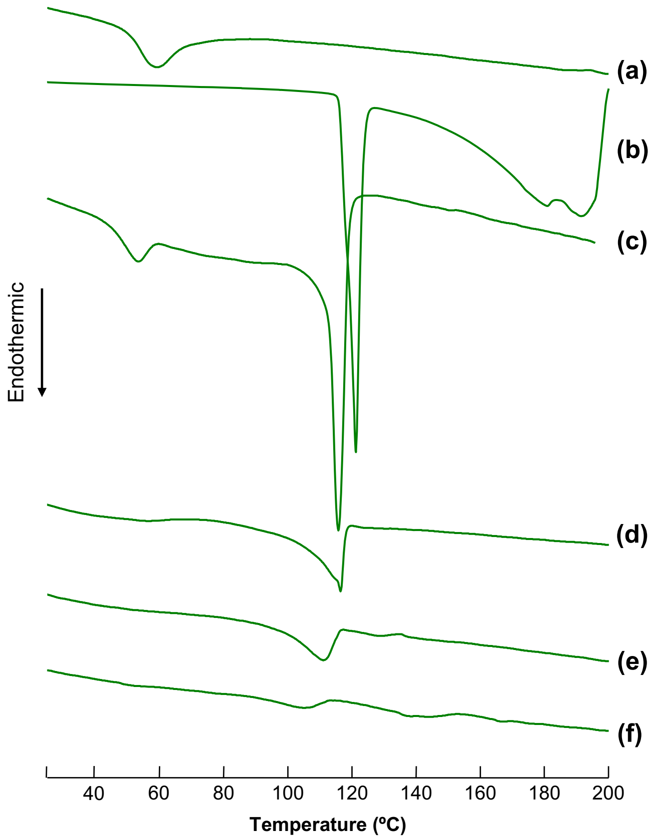

Fig. 3. DSC curves of SHL (a), SUC (b), SHL–SUC PM (c), and SHL–SUC AM (annealing for 1 h (d), 6 h (e) and 24 h (f) without washing).

the increment of relative peak intensity at 1737 cm^{-1} which was assigned as carbonyl stretching was observed, confirming the succinate formation (FTIR peak assignment of shellac succinate is proposed in Fig. 4).

3.1.4. NMR spectroscopy

To confirm the esterification between SHL and SUC, the NMR spectra of SHL–SUC were recorded and comparatively evaluated with SHL. All of the resonances attributable to the SHL were presented in the ^{1}H NMR spectrum (Fig. 5a). The ^{1}H NMR spectrum of SHL–SUC 24 h AM was virtually superimposed on those observed for SHL. The most significant change was the loss of the relative resonance of the peaks observed for the methylene group (–CH_2–OH) at δ_H 3.49 ppm and for the methine (–CH–OH) at 3.25 ppm and the addition of resonance attributable to an oxygenated methylene group of SHL–SUC at δ_H 3.96 ppm. Furthermore, the presence of succinyl side chain was indicated as observed by the signal from additional methylene group at δ_H 2.46 ppm. The finding was also supported by ^{13}C NMR spectra. The increment of the number of signals, assumed to the carbonyl stretching of succinyl (δ_C 168–178 ppm), was clearly observed on the spectrum of SHL–SUC 24 h AM (data not shown). From the results above, it should be reasonable to conclude that the formation of shellac succinate was accomplished after annealing.

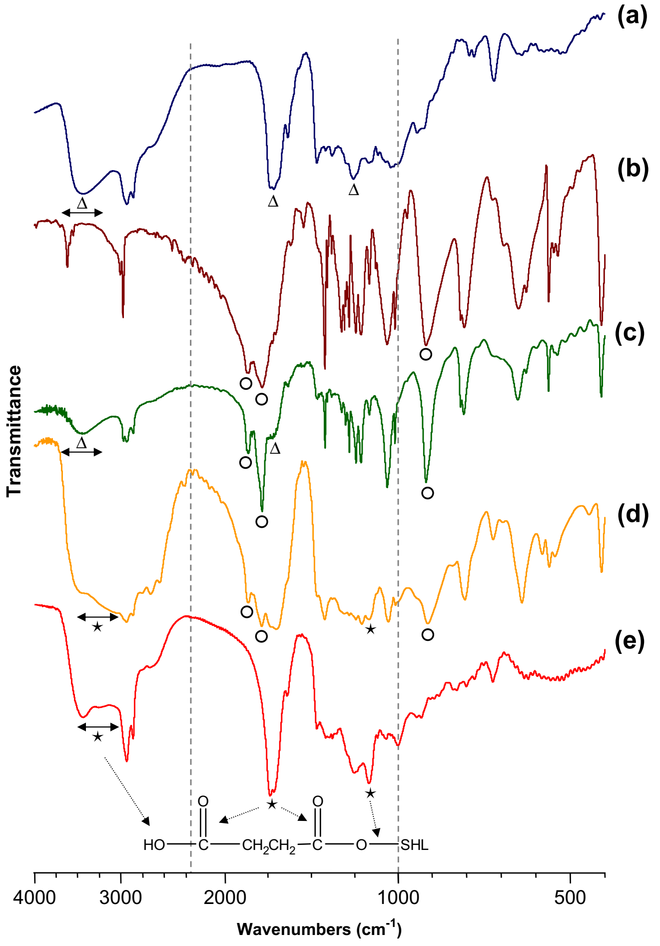

Fig. 4. FTIR spectra of SHL (a), SUC (b), SHL–SUC PM (c) SHL–SUC 24 h AM before washing (d), and SHL–SUC 24 h AM after washing (e).

3.2. Characterization of film

In order to study the film properties of shellac succinate, SHL–SUC AM films which were varied in acid value, were prepared. Clear films of all shellac samples were successfully cast from ammoniated aqueous solution. The films were then comparatively evaluated for water vapor permeability, mechanical property and pH solubility profile.

3.2.1. Water vapor permeability of film

The important characteristic of shellac film is a low water vapor permeability (WVP), comparing to other enteric polymers [2]. Since the reaction affected molecular structure of shellac by increasing the succinate moieties, we also determined whether the WVP of films changed by succinate formation. Fig. 6 demonstrated the WVP coefficient of SHL, SHL–SUC 1 h AM, SHL–SUC 6 h AM, and SHL–SUC 24 h AM. The SHL showed slightly lower WVP coefficient as compared to SHL–SUC AM

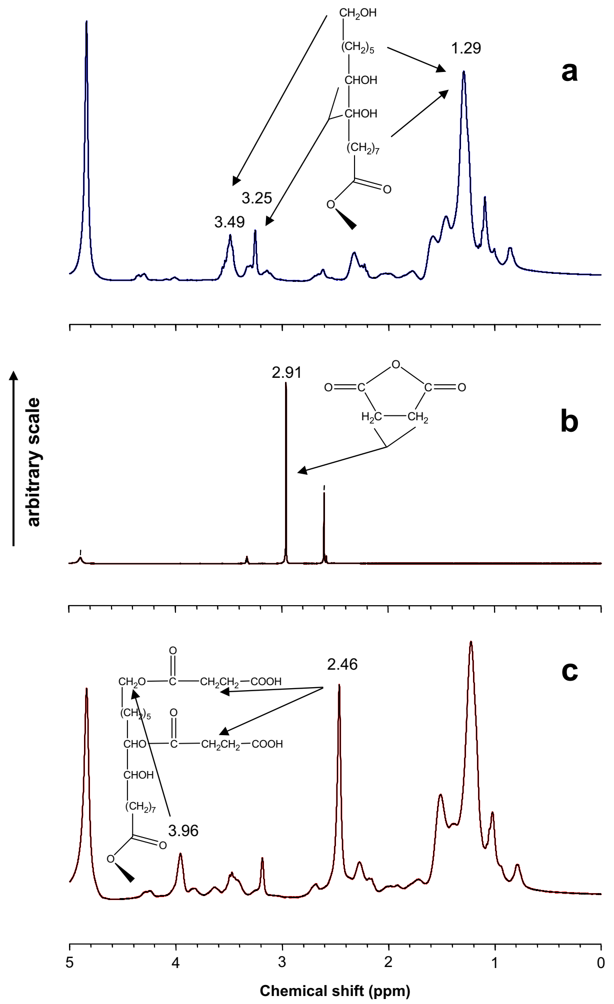

Fig. 5. ^{1}H NMR spectra of SHL (a), SUC (b), and SHL–SUC 24 h AM (c).

($p = 0.05$). The result suggested that the change of WVP was slightly affected by the increase of succinate moieties.

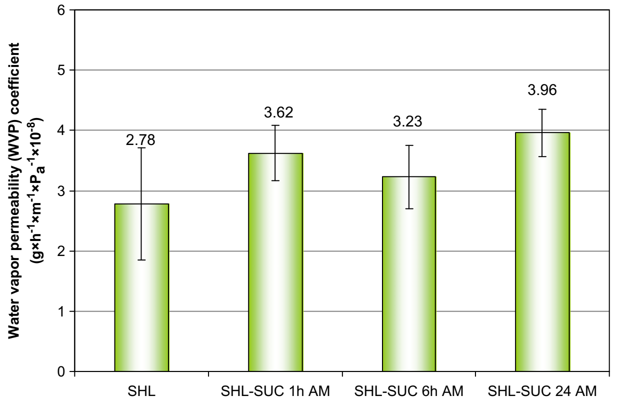

Fig. 6. WVP coefficient of films prepared from SHL, SHL–SUC 1 h AM, SHL–SUC 6 h AM and SHL–SUC 24 h AM.

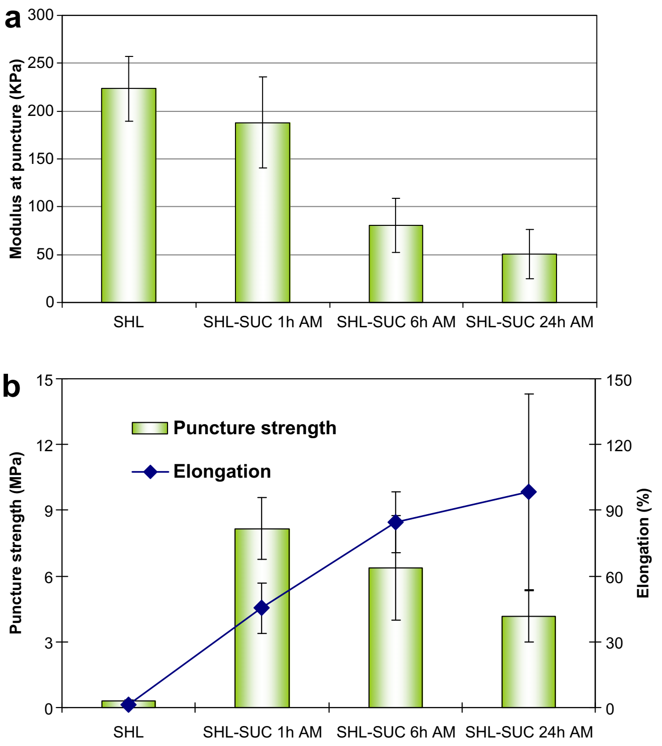

Fig. 7. Mechanical properties of films prepared from SHL, SHL–SUC 1 h AM, SHL–SUC 6 h AM, and SHL–SUC 24 h AM.

Several studies reported that WVP was dependent on the solubility or hydrophilicity of film formers and added excipients. Generally, higher the aqueous solubility or hydrophilicity, higher the WVP coefficient is. For example, Eudragit RL exhibited higher WVP than Eudragit RS since it contained more groups of hydrophilic quaternary ammonium [30]. Adding of plasticizers, e.g., glycerol, sorbitol, and propylene glycol, had increased the WVP of films prepared from various polymers due to the high aqueous solubility [31,32]. Therefore, the increase of more hydrophilic carboxylic groups by succinate formation might promote the permeation of water through the film in the same way. However, the increment of WVP was not too high to deteriorate the important advantage of shellac. The WVP coefficient of shellac succinate was still in a low level as compared to the reported values (1×10^{-7} to 3×10^{-5} $g\,h^{-1}\,m^{-1}\,Pa^{-1}$) of several enteric polymers, including cellulose acetate phthalate (CAP), hydroxypropyl methylcellulose phthalate (HPMCP, HP-55), hydroxypropyl methylcellulose acetate succinate (HPMCAS, AS-LG), and methacrylic acid–ethyl acrylate copolymer (Eudragit L30D) [33–36].

3.2.2. Mechanical properties of film

The change of mechanical properties of shellac film by various organic acids [4], plasticizers [37] and polymers [38] has been reported. Since the succinate formation might also affect the mechanical properties, we comparatively evaluated puncture strength, elongation at puncture and modulus at puncture of shellac films. The modulus at puncture of SHL was about 243 kPa. With the increase of annealing time, the modulus had a tendency to decline

(Fig. 7a). Since the modulus expressed the rigidity of film, the succinate formation led to the decreased stiffness. The data were supported by the elongation at puncture. SHL showed very brittle characteristic as indicated by the low percentage of elongation (Fig. 7b). With succinate formation, the percentage of elongation increased significantly ($p < 0.01$), suggesting the increment of ductile behavior of the films. The puncture strength of shellac succinate films was higher as compared to SHL film. The fragility of SHL film might cause the low puncture strength although the modulus was high as compared to shellac succinate films. With the increase of the succinate moieties, the puncture strength was decreased. From all the results above, the succinate formation could significantly increase the flexibility of film although the softer film was observed.

Generally, the addition of plasticizers increases the elongation of film, but it is also often involved in the reduction of strength and modulus. Various plasticizers, including triethyl citrate and polyethylene glycol, could change the mechanical properties of shellac film [4,37]. However, the causes for the modified mechanical properties of shellac succinate films were considered to be different since the plasticizer free films were prepared. With regard to the permeability of water as shown in Fig. 6, the WVP increased as succinate formation increased. Therefore, it would be possible that water could act as a plasticizer, resulting in change of mechanical properties with the increase of succinate formation. Similar plasticization effects of water have been reported [39,40]. Another possibility would relate to the interaction between polymer chains of shellac. The presence of functional groups in a polymer determined various types of interactions which consequently affected the mechanical properties of films [40]. Since succinate moieties possessed extra carboxyl groups, the different hydrogen bonding could occur and affect the inter-chain interaction of shellac. Different hydrogen bond scheme between SHL and shellac succinate was supported by the change of O–H stretching as observed in the FTIR spectra (Fig. 4a and e). In addition, the more steric effect of the succinate group might also cause the polymer chains to separate from each other, resulting in a change of mechanical properties.

3.2.3. pH solubility profiles of films

The main function of the enteric film is to protect the product from gastric environment and to dissolve promptly after the product reaches the small intestine. The native shellac possesses very good gastric resistance whereas low solubility at the pH of small intestine is still a problem. In order to evaluate the enteric property of shellac succinate, we comparatively determined the pH solubility profile of shellac succinate with that of native shellac. At first, each shellac sample was soaked in SGF for 2 h and then transferred to the buffer solutions at various pH values for 3 h. All shellac samples showed low percentage dissolved in SGF, although slightly increased percentage dissolved was observed as succinate formation increased (less than 5%), indicating the gastric resistance. The percentage dissolved of shellac films after soaking at various pH values is demonstrated in Fig. 8a. The percentage dissolved of all films increased with the increase of pH values. SHL and SHL–SUC 1 h AM films were completely dissolved at pH 7.0. With extended annealing time, the percentage dissolved increased. The pH, at which films were completely dissolved, was observed at a lower value (e.g., 6.4 and 6.1 for SHL–SUC 6 h AM and SHL–SUC 24 h AM films, respectively). Additionally, we also determined the dissolving time at which all films were dissolved (pH 7.0). The dissolving time of films decreased as annealing time increased, especially in the first 1 h (Fig. 8b). The result supported the improved solubility of shellac succinate films at intestinal pH. The succinate formation not only increased the percentage of dissolved shellac at lower pH but also increased the rate of dissolution at higher pH.

As previously described in Section 3.1, the increment of carboxylic acid was observed after the succinate formation. Similar result was also observed after increment of carboxylic acid groups with other enteric polymers [15,34,35,41]. Therefore, it was reasonable to conclude that the solubility enhancement was due to the increment of carboxylic acid moieties of succinate moieties.

Fig. 9 demonstrated the proposed diagram of succinate formation and its consequence on the properties of films. As supported by the FTIR and NMR spectroscopy, the succinic anhydride was esterified at the OH groups of shel-

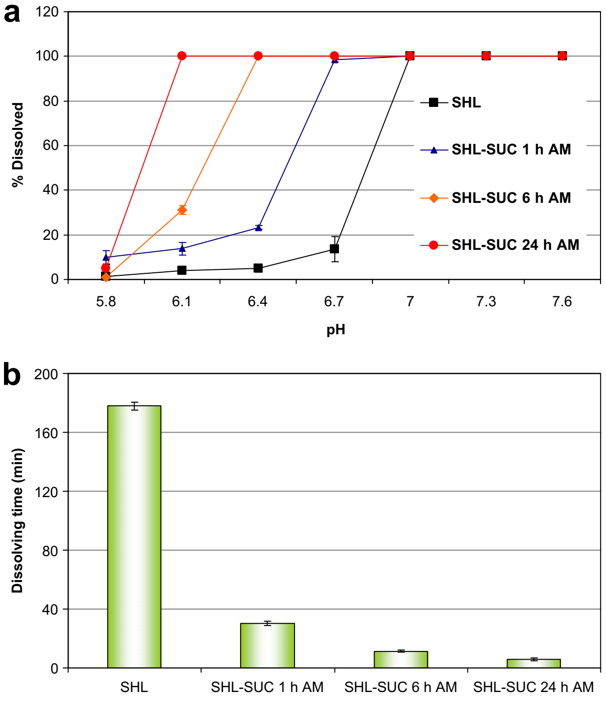

Fig. 8. pH solubility profiles (a) and dissolving time at pH 7.0 (b) of SHL, SHL–SUC 1 h AM, SHL–SUC 6 h AM, and SHL–SUC 24 h AM.

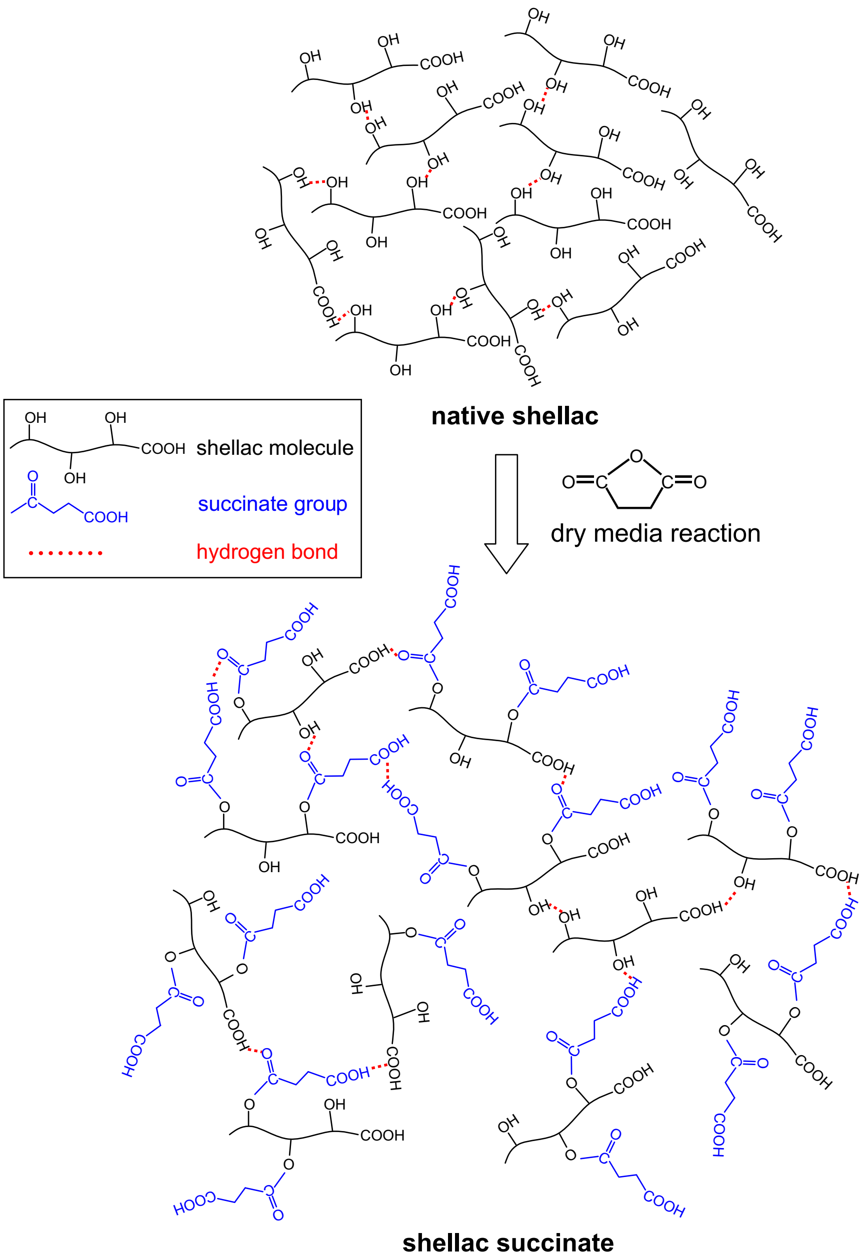

Fig. 9. Proposed diagram of succinate formation and molecular arrangement of shellac and shellac succinate.

lac molecules. The increment of carboxyl groups from succinate moieties was responsible for the solubility improvement. The change of mechanical properties of shellac succinate was assumed to involve with the different molecular arrangement as compared to native shellac. For native shellac, the polymer chains might strongly interact via hydrogen bonds and located close together, resulting in high modulus of elasticity or rigidity characteristic. With succinate formation, the succinate moieties could provide a steric hindrance that made the shellac polymer chains move apart and increase the free volume between the polymeric chains, causing more flexibility. The molecular arrangement of shellac succinate should be further stabilized by the new hydrogen bond schemes.

4. Conclusion

The formation of shellac succinate was easily achieved through organic solvent free reaction. The succinate moieties were esterified at the O–H groups of shellac molecules, which were supported by various characterization techniques. The increased amount of succinate moieties to shellac polymer significantly affected the film properties. The film prepared from shellac succinate was more flexible, although the loss of modulus was observed. Additionally, the enhanced aqueous solubility, especially at the pH of small intestine, was clearly observed. Varying amount of succinate moieties, as expressed by acid value, could be done to achieve the specified film properties. The finding could give an alternative way, which is simple, safe and efficient, to improve enteric properties of shellac.

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