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Fabrication of thermally stabilized shellac through solid state reaction with phthalic anhydride

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ABSTRACT

Shellac has been regarded as an obsolete polymer due to its poor thermal stability. The purpose of the study was to solve the problem by solid-state synthesis of shellac phthalate (SHL–PHT). Shellac was ground with phthalic anhydride and then thermally activated at various conditions. The solid-state esterification of shellac was clearly observed after annealing. As indicated by an increase of acid value, the esterification was more pronounced after the increase of annealing temperature and time. The formation of SHL–PHT was confirmed by FTIR spectra and other characterization techniques. The SHL–PHT demonstrated to improve the thermal stability as compared to native shellac. After aging at high temperature, percent insoluble solid and acid value of the native shellac dramatically changed while those of SHL–PHT were relatively the same as initial value, especially for the more esterified SHL–PHT. The protection of hydroxyl groups of shellac by phthalate moieties might be a possible explanation for the improved stability. In conclusion, the study may give an eco-friendly way to synthesize the shellac derivatives for future applications.

1. Introduction

Solid-state reaction has been recognized as one of the fundamental importance in material science since it could offer an efficient way for inducing solid state transformation, including amorphization [1,2], complexation [3,4] and synthesis. During the past few decades, solid-state syntheses have attracted considerable attention because the reactions occur in the absence of toxic organic solvents and could provide higher yield in mild conditions [5]. Several materials, e.g., nickel hydroxide, iron phosphate, and composite oxides, have been successfully prepared by the solid state reaction [6–8]. However, most studies focused on the syntheses of inorganic materials while few studies investigated on organic compounds, especially polymers.

Shellac (SHL) is one of the polymers that has been applied in many industrial fields, e.g., food, agricultural, paint, cosmetic and pharmaceutical industries. As of nature origin and low water permeability, it could be used as a safe moisture barrier coating for fruits and pharmaceutical products [9,10]. However, the utilization of SHL has decreased because of its inadequate thermal stability. Self-polymerization of SHL via hydroxyl and carboxyl groups resulted in the aging problem. Several investigations have been carried out in recent years to solve this problem by modification of SHL molecules. The salt formation at carboxyl groups was proposed to inhibit the polymerization process [11,12]. However, the stability problem was not yet fully solved since the hydroxyl groups were not completely protected. Recently, we attempted to modify the hydroxyl groups by esterification with succinic anhydride [13]. Nevertheless, the stability problem was not absolutely solved. Therefore, further investigations are still needed in order to overcome the degradation problem of SHL.

The aim of the present study was to synthesize SHL derivative via solid-state esterification using phthalic anhydride (PHTA). The effect of annealing process on formation of shellac phthalate (SHL–PHT) was monitored by several characterization techniques. In addition, the thermal degradation study was also conducted to compare SHL with SHL–PHT.

2. Material and methods

2.1. Material

SHL was purchased from Thananchai Part., Ltd. (Bangkok, Thailand). PHTA was obtained from Merck (Darmstadt, Germany). All chemicals were of analytical grade or pharmaceutical grade.

2.2. Preparation of shellac phthalate by solid-state reaction

An accurate weight of SHL and PHTA in a 1:4 molar ratio was ground in a planetary ball mill (PM 100, Retsch, Germany) for 90 min.

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In order to control the temperature to lower than 40 °C, the mill was periodically paused and the grinding cell was cooled. The ground mixture was then annealed at 60, 80 and 100 °C for 12 h. In addition, the effect of annealing time was studied by annealing at 80 °C for 1, 6, 12 and 24 h. After annealing, the mixture was removed and immediately washed with purified water to remove excess PHTA. A part of annealed mixtures (without washing) was also collected for comparative characterization.

2.3. Characterization of shellac phthalate

The formation of SHL–PHT was monitored by determination of acid value which was previously described [14,15]. Briefly, shellac sample was dissolved in ethanol, centrifuged and filtered through filter paper. The filtrate was potentiometrically titrated with 0.1 N sodium hydroxide VS. The insoluble solid on filter paper was washed with excess ethanol and dried at 70 °C until the weight was constant, and then the percentage of insoluble solid was calculated. Other characterization methods were performed by the following conditions. FTIR spectra of SHL samples were recorded with an FTIR spectrophotometer (Nicolet 4700, Thermo Electron Corporation, USA) using the KBr disk method from 4000 to 400 cm^{-1}. The differential scanning calorimetry (DSC) curves were recorded by a differential scanning calorimeter (Sapphire, Perkin Elmer, Japan) at the heating rate of 10 °C/min. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (Ettlingen, Germany), using residual methanol peaks at δ_H 4.84 and at δ_c 49.05 ppm as chemical shift reference signals.

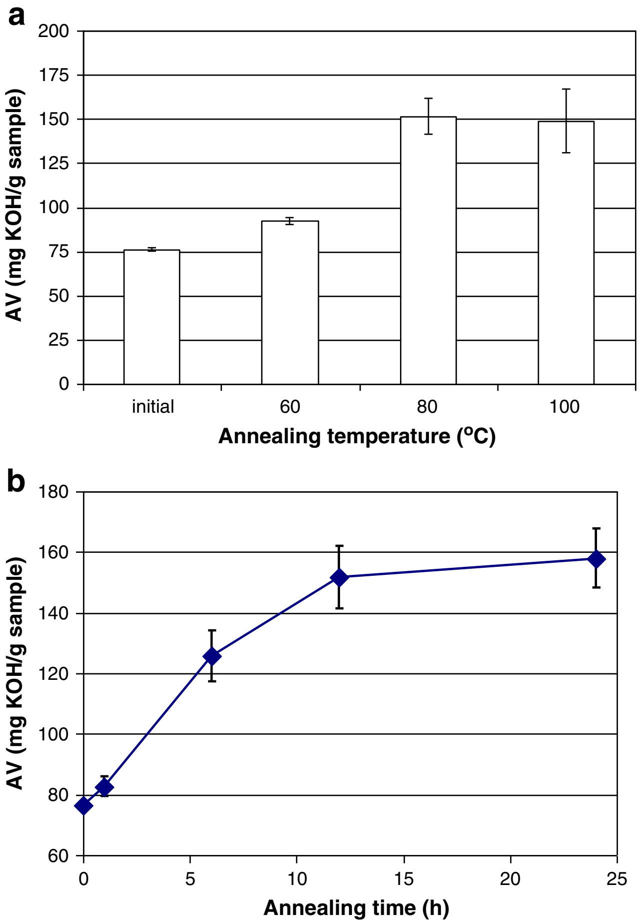

Fig. 1. Effect of annealing conditions on acid value of shellac samples: (a) annealing at various temperatures for 12 h, (b) annealing at 80 °C for 1, 6, 12 and 24 h.

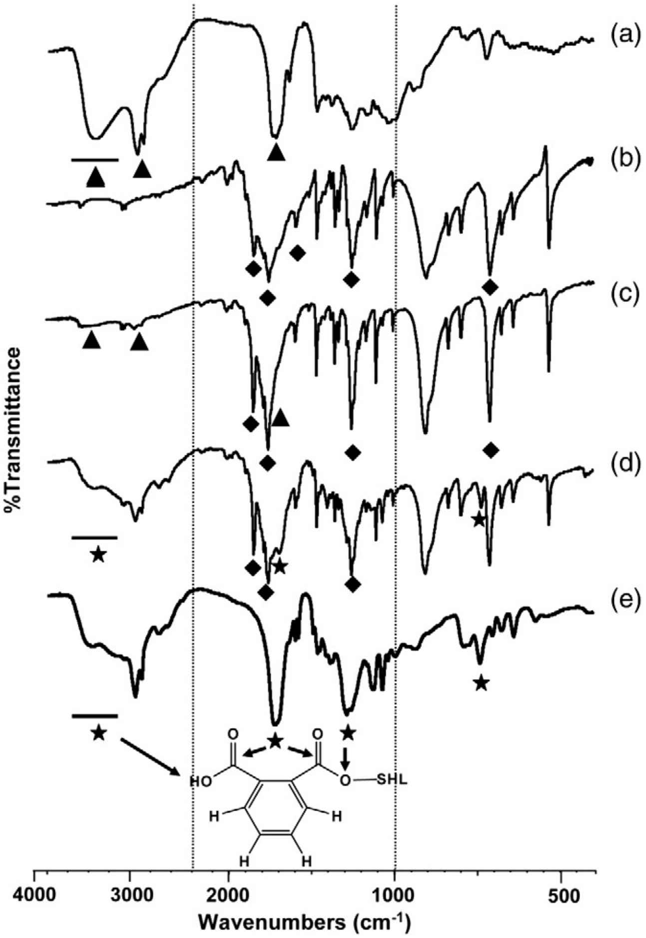

Fig. 2. FTIR spectra of (a) SHL, (b) PHTA, (c) SHL–PHT GM, (d) SHL–PHT AM 12 h before washing and (e) SHL–PHT AM 12 h after washing.

2.4. Accelerated thermal degradation test

SHL and SHL–PHT were heated at 80 °C for 24 h. The heated samples were then dissolved in 95% ethanol overnight. The acid value and insoluble solid of all samples were determined by the methods described in Section 2.3.

3. Results and discussion

3.1. Solid state formation of shellac phthalate

SHT–PHT was synthesized by solid-state esterification with thermal activation. Acid value, which represented the amount of carboxylic acid per gram of material, was used as an indicating parameter for monitoring the increased carboxyl groups after phthalate formation. Fig. 1 demonstrates the effect of annealing temperature and time on acid value of SHL samples. The acid value was significantly increased after annealing at 60 °C or more. The annealed mixture (AM) at 80 °C showed a 2-fold increase of acid value, as compared to native SHL. The increase of temperature to 100 °C did not remarkably promote the reaction; therefore, we selected the reaction temperature of 80 °C for further study. As the annealing time increased, the acid value was gradually increased and the value almost reached the plateau after heat treatment for 12 h (Fig. 1b). The increment of acid value suggested that phthalate moieties were successfully reacted at the hydroxyl groups of SHL molecules. Moreover, the desired acid value could be achieved