The effect of polyethylene glycol on shellac stability

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Abstract. The effect of polyethylene glycol (PEG) having a molecular weight of 1000 and 2000 on shellac stability has been investigated in this research. The shellac was shellac wax free, and the solvent was ethanol 96 %. Shellac films were prepared by solvent evaporation method. The stability of shellac was investigated using insoluble solid test, Fourier Transform Infra Red (FTIR), Thermogravimetry Analyzer (TGA), and Water Vapour Transmission Rate (WVTR). The results showed that stability of shellac decreased after heating at 125°C for 10, 30, 90, and 180 minutes, and storing for 1 month at 27°C and 85 relative humidity (RH). PEG improved the stability, and the most stable effect was achieved through PEG1000.

1. Introduction

Shellac is a natural polymer produced by insects in the forest in tropical countries. It is non-toxic, renewable and naturally decomposable so its products could meet sustainable and environmental protection requirements. It had been applied in food and medicine coating, metallurgy, military, etc. The attractive of shellac use relied on its; high adhesive strength, great electrical insulation property, waterproofness, moisture and corrosion resistance, ultraviolet screening, oil resistance, enteric nature (acid resistance) and good dye-fixing.

However, shellac also has disadvantages relating to its stability. Over time its molecular groups could undergo intramolecular chemical bonding (polymerization) which led to changes in its properties, it becomes more brittle and less soluble. Shellac underwent polymerization/aging by either heating or exposure to humidity [1]. Since most of the acids contained more than one hydroxyl group and some more than one carboxyl group it was believed that this polymerization was a result of self-esterification of the material as shown in the proposed mechanism by Limmatpavirat [2] in Figure 1. This polymerization manifested itself in the so-called blocking of the material as the individual shellac flakes stuck together. Hence, the stability of shellac could be improved by protecting these functional groups [2,3]. The amount of polymerization in shellac correlated to the percentage of insoluble solid.
Several attempts have been done to address this issue. Alkali treatment of shellac and thus composite salt formation (by carboxylate ions) improved flexibility and stability but worsen water barrier properties [4]. A comparison between native and hydrolysed shellacs prepared as films in free acid and ammonium salt forms by using ethanol and ammonium hydroxide solution, respectively, did show that alkali treatment increased acid value, solubility at pH 7 and strain, but decreased ester value, water vapour permeability coefficient and stress. The composite salt formation also led to the stabilisation of shellac [3-6], which was believed to occur through the protection of polymerisable groups and stopped the formation of esters through the reversal of the salt formation mechanism (a known aging effect). This can extend the shelf-life of films from 3 to over 12 months when stored at 40 °C and 75%RH. Although composite salt formation provided flexibility to shellac films and coatings, plasticizers were still required to overcome their brittleness. Although this could lead to poorer water barrier properties, plasticizers also served to protect shellac from polymerisation and thus stabilized their properties, this was believed to occur through a hydrogen bonding mechanism which protected the reactive groups. Anan et al. [7] showed that PEG with Mw of 400 was better than that of 200 and 4000 and reasoned it to the balance between a number of hydrogen bonding environments and molecular volume. An investigation to look at Mw 1000 and 2000 is deemed necessary as these may provide further stabilization. The high Mw are less likely to migrate or leach from polymerisable sites and thus, lead to higher stable films, however too high an MW will lead to poor plasticising effects. Other plasticizers such as triacetin or diethyl phthalate provided less stability.

2. Experimental

2.1. Materials
Shellac wax free was supplied by Sigma-Aldrich UK. Alcohol 96 % was supplied by Merck Germany. Plasticizer polyethylene glycol was supplied by Sigma-Aldrich UK.
2.2. Preparation of shellac and plasticised shellac films

All films presented were prepared by solution casting. Shellac films were made by dissolving 1.25 gr of shellac in 12.5 ml ethanol (96%) while PEG/shellac films (10 wt%) were prepared by mixing and stirring shellac solution and PEG solution. The shellac solutions were made by dissolving 1.125 gr of shellac in 10 ml ethanol and stirred for 2 hours while PEG solutions were made by dissolving 0.125 gr of PEG in 2.5 ml ethanol and stirred for 2 hours using a magnetic bar/stirrer at room temperature. The solution was then cast into Petri dish, then dried at 50 °C for 7 hours before being analysed.

2.3. Characterization

2.3.1. Insoluble solid. Polymerisation of shellac was accelerated by heating at 125°C for 10, 30, 90, 180 and 360 minutes. The heated shellac film was dissolved in ethanol (96%) for 3 hours. The solution was then filtered using a metal filter (150 mesh). The insoluble solid was dried at room temperature until a constant weight was obtained and the percentage calculated.

2.3.2. Fourier Transform Infra Red (FTIR). A Thermo Nicolet NEXUS spectrometer along with an MCT (mercury cadmium telluride) detector cooled by liquid nitrogen was used for all the FTIR analysis. The spectrometer was coupled with a single reflection diamond ATR cell (GrasebySpecac, U.K). This setup has the trade name "Golden Gate". The film was placed on top of the crystal diamond and the spectra of the films taken. The wavelength of interest ranged from 700 to 4000 cm⁻¹ and was collected with a resolution of 4 cm⁻¹ and 64 scans. Omnic software was used to collect and analyse the spectra.

2.3.3. Thermogravimetry Analyzer (TGA). All TGA measurements were performed on a Mettler Toledo TG50 Thermogravimetric Analyser using an alumina crucible. Data was recorded at a heating rate of 20 °C/min between 35 and 800 °C after an initial isothermal stage where the sample was kept at 35 °C for 15 minutes. The analysis was performed under a nitrogen atmosphere with a flow rate of 10 ml/min.

2.3.4. Water vapour transmission rate (WVTR). An experimental procedure to measure the WVTR was conducted using aluminium Payne cups (supplied by Sheen Instruments) with exposed surface area of 10 cm² and containing silica gel desiccant (8 g in each cup), which is closed by the material to be tested and dried overnight in an oven at 100 °C. The cups were placed in a controlled atmosphere (humidity chamber). The cups were weighed at suitable time intervals and the WVTR were determined from the increase in mass when this increase had become proportional to the time interval. The WVTR result was calculated from the equation (1) [8].

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\text{WVTR} = \frac{(240 \times m)}{(S \times t)}
\]

where is the total duration in hours, m is the increase in mass in milligrams of the assembly during the time t, and S is surface area exposed by the Payne cups. Shellac and PEG/shellac films were equilibrated in the humidity oven at 23 °C and 85 % relative humidity (RH) for 24 hours before performing the WVTR measurement. The relative humidities of 85% were achieved by placing saturated potassium chloride salt solutions, in a humidity chamber [9].

3. Result and Discussion

Figure 2 shows the insoluble solid of both native shellac (no PEG presence in shellac) and shellac plasticized by PEG of different molecular weight after heating at 125 °C for a different time, i.e., 10, 30, 90, 180, 360 minutes. It shows that the insoluble solid increases with increasing heating time are indicating that the degree of polymerization increases with increasing heating time for both native shellac and plasticized shellacs. When samples were heated, the energy will break the carboxyl bond.
to create ester. The longer the heating, the higher amount of ester produced. These results suggest that plasticizer polyethylene glycol improved the stability of shellac although it did not stop polymerization of shellac. The O-H group of PEG may protect the carboxyl group of shellac resulting in bonding in PEG/shellac is stronger than that of shellac. A similar trend of the insoluble solid test was also reported by Anan [7] using PEG200, 4000, and 4000. It also showed that PEG1000 gave the most stable effect on protecting of shellac compared to PEG2000. The amount of carboxyl group that can be protected by PEG1000 may be higher than that of PEG2000 as PEG2000 has longer molecular chains.

![Figure 2](image)

**Figure 2.** Effect of PEG on shellac stability via insoluble

Identification of shellac polymerization using FTIR has not been reported so far in the literature. According to proposed mechanism in Figure 1, polymerization of shellac is thus assigned by the increase of peak intensity bands of C=O stretching of ester 1709 cm\(^{-1}\) and the decrease of as O-H stretching of the hydroxyl group at 3400 cm\(^{-1}\). The intensity of the band at 2942 cm\(^{-1}\) occurs due to the C-H stretching vibration [10] and does not change with a change in the degree of shellac polymerization. Therefore, the intensity ratios of the band of O-H cm\(^{-1}\) to C-H, and the intensity ratios of the band of C=O to C-H from all films then correlates to the polymerization in shellac.

Typical FTIR spectrum of shellac, PEG1000/shellac (10 wt%), and PEG2000/shellac (10 wt%) after heating is shown in Figure 3 giving the information of peak intensity bands of C=O, O-H, and C-H due to heating. The peak intensities of O-H to C-H and C=O to C-H were rationed, and the results are given in Figure 4 and Figure 5, respectively. It showed that the peak intensity ratios of O-H to C-H decreased while the peak intensity ratio of C=O to C-H increased indicating that polymerization occurred in shellac and plasticized shellac supporting insoluble solid test in Figure 1. The rate of peak intensity ratio of O-H to C-H and C=O to C-H is the smallest in PEG1000/shellac, followed by PEG2000/shellac, and shellac.
Figure 3. FTIR spectrum of shellac and PEG shellac system heated at 125 °C for 30 minutes.

Figure 4. Peak intensity band of O-H of shellac, PEG1000/shellac, and PEG2000/shellac after heating at 125 °C for 0, 30, 90, and 180 minutes.
Figure 5. Peak intensity band of O-H of shellac, PEG1000/shellac, and PEG2000/shellac after heating at 125 °C for 0, 30, 90, and 180 minutes.

The thermograms collected from the shellac, PEG1000/shellac, and PEG2000/shellac is presented in Figure 6. In general, there are 3 areas of weight loss. The first weight losses observed in the range 35-150 °C relates to water or solvent present in the sample. The second weight losses observed in the range 250 – 475 °C relates to structural decomposition of the shellac. Above 500 °C, relatively little weight is lost which relates to remained compound or carbon. The TGA data shows that adding PEG improved thermal degradation of shellac. PEG1000 increased thermal degradation temperature of shellac by 20 °C compared to only 5 °C by PEG2000.

The water vapour transmission rate (WVTR) of shellac, PEG1000/shellac, and PEG2000/shellac collected at day 0 (samples were prepared), and after 1 month is given in Figure 7. Lower WVTR correlates to good water vapour barrier properties, and vice versa. It shows that adding PEG reduces water vapour barrier properties of shellac. PEG may break hydrogen bond between molecular chains of shellac, in addition to hydrophilic properties of PEG. Generally, PEG reduces water vapour barrier properties of the polymer [10]. The decrease of water barrier properties was higher due to PEG2000 than that of PEG1000. Furthermore, the water vapour barrier properties decreased after one-month storage in 85 %RH indicating either polymerization or penetration of water vapour into shellac chains reduced the water barrier properties of shellac.
4. Conclusion
It has been shown that polymerization in shellac and plasticized shellac occurred by heating the samples at 125 °C. The percentage of the polymerization is increased with heating time as shown by
the insoluble solid test. The polymerization was slowed down by PEG, and the most stable effect was given by PEG1000. The trend of polymerization was confirmed by FTIR as shown by the decrease of the peak intensity ratios of the O-H band to C-H band, and the increase of intensity ratio of C=O band to C-H band. Adding PEG1000 and PEG2000 also increased thermal degradation temperature of shellac up to 20 °C and 5 °C, respectively. The water vapour barrier properties of shellac decreased both after adding PEG and stored for 1 month at 85 % RH at 27°C.

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