Effects of combined chlorine on physicochemical properties and structure of shellac

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Abstract: The objective of this work was studying the effects of combined chlorine on the physicochemical properties and the structure of shellac. Bleached shellacs with different chlorine content were prepared by means of elimination reaction which sodium ethoxide was used as nucleophilic reagent. Then polymerization time and iodine value characterizing the quality of shellac were tested for investigating the relationship between the physicochemical properties and chlorine. The mechanism of dechlorination of shellac was analyzed, and the structures of products were characterized with the aid of ultraviolet spectrophotometer. It was demonstrated that the polymerization time become long and the value of double bond become large with the decrease of chlorine combined in shellac molecule, and that the properties of shellac with low chlorine content had been improved. The structure of shellac obtained by means of dechlorination was different from that of product without dechlorination.

Keywords: Biomaterials, coatings, shellac, natural products, polymer.

INTRODUCTION

Shellac, a natural resin, has been the focus of interest due to its outstanding character, such as non-toxic property, non-irritating performance, excellent film forming behavior, and good acid-resistant features etc (Farag, 2011). It is widely used in national defense, electroengineering, and coatings etc. After bleached with NaClO to remove Lac pigment and Lac wax, the resin is also widely used in pharmaceutical industry (Felix, 199; Nadian and Lindblom, 2002; Pearnchob *et al.,* 2003; Pearnchob *et al.*, 2004; Pearnchob and Bodmeier, 2003), food field (Tang, 2003), and fruits refreshing domains (Bai *et al.,* 2003; Fallik *et al.,* 2005; Hagenmaier, 2000; Hagenmaier, 2002; Hagenmaier, 2005; Pearnchob, *et al.,* 2004; Sarisuta *et al.*, 1999; Trenktrog *et al.,* 1996; Valencia Chamorro *et al.,* 2009). However in the bleaching process chlorine is added to the double-bond structure of shellac molecule, then combined chlorine is formed. The polymerization existing among inner molecule of shellac is catalyzed by the chlorine, and poor storage performance of shellac is attributed to the catalysis of combined chlorine. In fact the shelf time of shellac is less than six months, and moreover the existence of chlorine combined with shellac limits its application in pharmaceutical and food industry.

The chlorine content of bleached shellac in domestic is higher than that of products in abroad, and it is much higher than that of products required by the food and pharmaceuticals. Therefore the domestic product is currently not used in food and pharmaceutical industry, and the shellac for making enteric-coated capsules of drug can be only relied on imports. Some reasons could account for the variation of chlorine content in bleached shellac in different products. One reason is that there are some difference in the composition and structure of seedlac used for preparing shellac (Liao *et al.,* 2007). Another is that the parameters used for controlling the bleaching process are protected as know-how by manufacturers.

During the process of shellac being bleached, the more the amount of bleaching agent is used, the lighter the product's color is and the more chlorine it contains. But with the more chlorine the product contains, the poorer the storage performance is. For avoiding these negative effects of combined chlorine some study which shellac are bleached with comprehensive bleaching agent or other bleaching agent without chlorine have been carried out. However compared to the sodium hypochlorite, not only the bleaching property is inferior, but also other harmful substances are induced to shellac when these kinds of bleaching agents are used. Some studies involving in how to eliminate the combined chlorine in shellac have been reported. WANG prepared shellac with a chlorine content 0.63 wt% with the aid of dechlorination agent and studied the mechanism of chlorine removal by adding dechlorination agent in shellac-bleached solution (Wang *et al.,* 1987). Liao *et al*. prepared shellac with chlorine content less than 0.5 wt% by means of adding binary metal catalysts that Pd and Ni are used as active ingredient (Liao and Chai, 2008; Liao *et al.,* 2009; Liao *et al.,* 2011). When it reacts with catalysts, the chlorine combined in products is dissociated by means of catalytic hydrogenation.

However few studies involving in the effects of combined chlorine on the thermal polymerization time, iodine value

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and variation of structure was reported. Polymerization time and double bond value (expressed by iodine value) of shellac are two important indicators characterizing the physicochemical properties of bleached shellac. In this work for obtaining products that have different chlorine content, sodium ethoxide is added to the bleached solution to eliminate the chlorine combined in shellac structure while it is bleached. The effecting relationships of chlorine on physicochemical properties of shellac are revealed with the aid of origin software, and the structure of shellac affected by combined chlorine is revealed.

MATERIALS AND METHODS

Materials

Materials used in this work were anhydrous ethanol, metal sodium, sodium carbonate, sulfuric acid, sodium hypochlorite and seedlac. Except sodium hypochlorite used was of industrial grade and provided friendly by Yunnan salt & saltchemical Co., Ltd. China. Seedlac was of industrial grade and purchased from Yunnan Mojiang Hongsen Special Agriculture Co., Ltd. China. The others were of analytical grade and purchased from Sinopharm chemical reagent Co., Ltd.

The experimental apparatus was shown in fig. 1. Low temperature pump (DLSB -5/10) and water recycling vacuum pump (SHZ-Dβ) were purchased from Gongyi yuhua instruments Co., Ltd. China. UV757 ultravoilet spectrophotometer (Shanghai precision-scientific instruments Co., Ltd., China) was used to determinate the structure of samples.

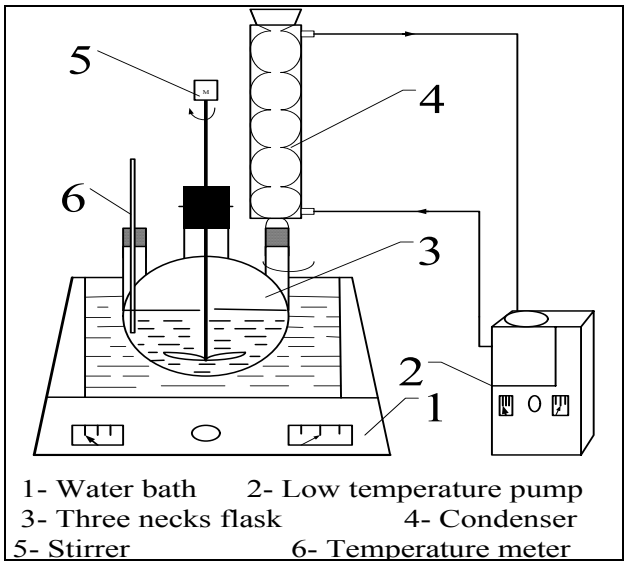

Fig.1: Sketch of experimental instrument

Preparation of bleached shellac with different chlorine

Fifty grams seedlac were dissolved in 250mL solution with a content of sodium carbonate 5% (w/w) at 90□ for 30 min, and seedlac alkaline solution was gotten after the branches, insects and other impurities contained by them were separated with stainless steel sieve. It was bleached with sodium hypochlorite solution with an effective chlorine concentration 3% (w/w) when seedlac alkaline solution was cooled down at a temperature 30□. After the color index of the bleaching solution was reached a specific value wanted, the process was stopped and the bleached solution was processed by means of two different methods. One was precipitated directly with a dilute sulfuric acid for obtaining shellac resin, and then it was treated routing as filtering, washing and drying to manufacture bleached shellac. The other was stirred at 90□ for different time in the presence of mixture of 4.05g sodium ethoxide with 30mL ethanol to eliminate the chlorine combined in the shellac molecule. After the process was completed, the reactant was cooled down to 30 degrees centigrade, and then dilute sulfuric acid was added to precipitate the resin. In the end the bleached shellac with different chlorine content could be got when the precipitation was filtered, washed and dried.

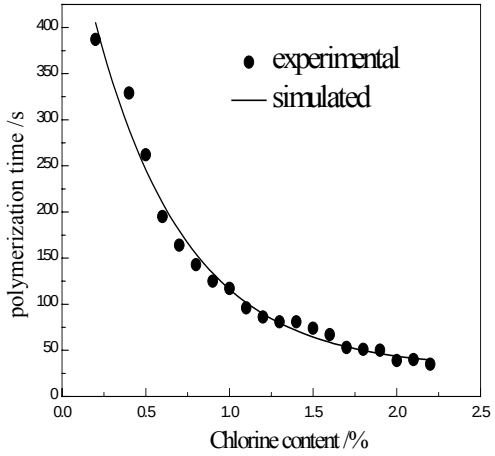

Fig. 2: Effect of chlorine on polymerization time

Physicochemical analysis of shellac samples

Chlorine content and physicochemical properties, including polymerization time, double bond value, were measured according to Lac products-testing methods GB/T8143-2008 (National standards administration committee of China, 2008). Chlorine in the sample was altered to soluble chloride by sodium, then silver nitrate and ammonium ferric sulfate were added in acidic conditions, and potassium sulfocyanate was used to titrate the chlorine content in the samples. Unsaturated double bonds could be characterized with iodine value by addition reaction in the sample. For detecting iodine value iodine bromide was added to react with the shellac in glacial acetic acid solution after the sample was dissolved in ethanol. Then the solution was titrated with sodium thiosulfate solution.

Ultraviolet spectrophotometer charactering

Ultraviolet spectrophotometer was employed to characterize the structure of seedlac the raw material used for preparation shellac, shellac without being dechlorinated, and shellac prepared by dechlorination in the presence of sodium ethoxide. The samples were dissolved in 95% alcohol (volume percentage) for a solution with concentration as 10μmol/L before scanned in UV 757 ultraviolet spectrophotometer.

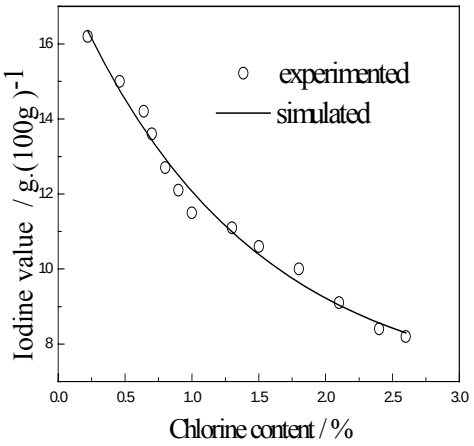

Fig. 3: Effect of chlorine on iodine value

RESULTS

Effect of chlorine content on polymerization time

The polymerization time of the product eliminated combined chlorine was different obviously, which could be shown in fig. 2. The polymerization can occur by the esterification among the functional groups in shellac molecules and cause the instability of shellac (Li, 2003). When the dechlorination process was not implemented, chlorine content of shellac products prepared from seedlac by bleaching modification with sodium hypochlorite was 2.2% (w/w), and its polymerization time was short just as 32s. The polymerization time was 117s when chlorine content was 1.0% (w/w), and it reached 329s while the value of chlorine content decreased by 0.4 wt%, and it could reach 387s when the chlorine content was 0.2% (w/w). The relationship between polymerization time and chlorine content was analyzed regressively using origin software, and it was found that the variation trends of polymerization time (P) versus chloride content (C) accorded with one first-order exponential decay model P=30.033+541.465exp (-C/0.544), and the model's regression coefficient R^2 equaled to 0.983.

Chlorine combined to shellac molecule in bleaching process is a significant factor influencing product's polymerization time. It is released out in the form of HCl during storage period, which can accelerate and catalyze the aggregation of shellac resin, and it not only shorts the polymerization time, but also limits its shelf life (Ha and Wang, 1997). The shorter polymerization time means the poorer storage performance of shellac products. The polymerition time becomes longer when the combined chlorine was eliminated. Generally the value of polymerization time of seedlac before being bleached is scattered in 300~450s (Liao and Chai, 2008). The polymerization time of shellac whose combined chlorine was eliminated is nearly the same value of the raw materials seedlac before it is used for preparing shellac.

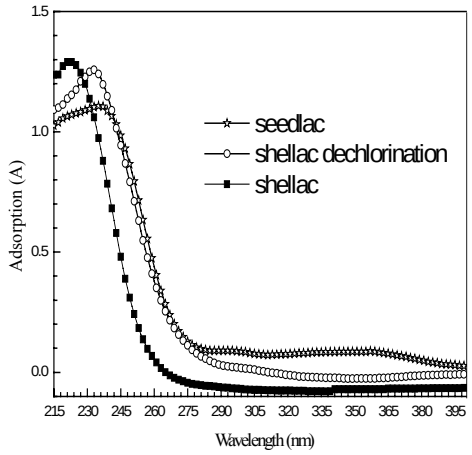

Fig. 4: Ultraviolet spectrum of samples

It could be drawn from the experimental results and discussion above that final products with different chlorine content can be got by eliminating chlorine for different time, and that with the decrease of chlorine in the product the polymerization time is increased and also that the smaller the chlorine content is, the longer the polymerization time is.

Effect of chlorine on iodine value

The effect of chlorine content on iodine value that could quantitatively characterize the unsaturated properties of products was shown in fig. 3.

It was observed from fig. 3 that the iodine value reaches more than 15 when chlorine content in bleached shellac was 0.5% (w/w) below, and that the iodine value only equaled to 8.2 when chlorine content in bleached shellac without being dechlorinated was 2.5% (w/w). To some extent, part of the combined chlorine was eliminated by 2.1% (w/w), then the iodine value increased by 10-11. The relationship between chlorine content and iodine value was analyzed regressively using origin software, and it was found that the variation trends of iodine value (I) versus chloride content (C) corresponded with one first-order exponential decay model I =6.658+11.423 exp (-C/1.339) and the model's regression coefficient R2 equaled to 0.986.

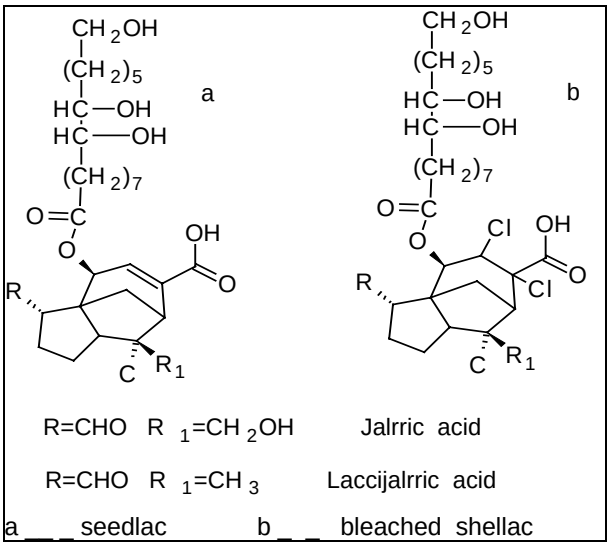

Fig. 5: Schematic diagram of bleached shellac structure

Effect of chlorine on structure of shellac

The samples of seedlac, shellac and shellac prepared by dechlorination which sodium ethoxide was used as nucleophilic reagent were respectively dissolved into ethanol 95% (volume %) and then scanned by ultraviolet spectrophotometer. The spectra were displayed in fig.4.

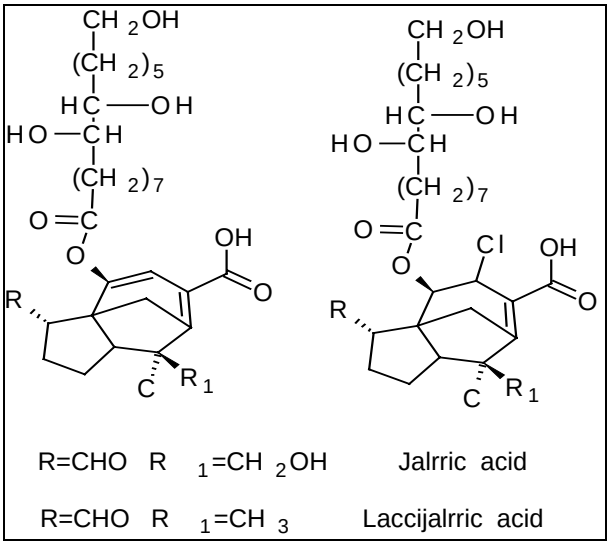

Fig. 6: The structures of shellac after dechlorination

It could be found that the maximum absorption peak of seedlac without being modified by sodium hypochlorite was 236 nm, and that, however, the maximum absorption peak of shellac which was prepared from seedlac by bleaching with sodium hypochorite shifted bluely to 222 nm. Accordingly, it also be shown from fig. 4 that the maximum absorption peak of shellac while it was processed by dechlorination by means of adding nucleophilic reagent was 235 nm, and it is nearly the same value as seedlac which was been used as raw material for preparing shellac.

To our knowledge, the maximum adsorption at 236 nm is due to the $\pi \rightarrow \pi^*$ transition of α、β- unsaturated carboxyl conjugated double bonds. There exists the $n \rightarrow \sigma^*$ transition of C-Cl while the C=C double bond is added by chlorine, and this is the reason that the maximum absorption peak shift blue. Why there is a feeble difference of the maximum absorption between the seedlac and the shellac being processed by dechlorination is due to except most of C=C bonds are recovered, there exist little $n \rightarrow \sigma^*$ promotion of C-Cl when most of combined chlorine are eliminated to form double bonds while dechlorination process was undertaken in present of sodium ethoxide. The result of ultraviolet spectrum of samples indicated the reasonableness of the structures of the seelac, shellac, and shellac being dechlorinated.

DISCUSSION

Seedlac consists mainly of a mixture of esters, its chemical structure is shown in fig. 5(a) (Limmatvapirat, 2004), and therefore it is regarded as an unsaturated polymer. Unsaturated organic compounds always have the molecular structure containing double or three bonds, and addition reaction can be produced by them. According to this specificity the index of unsaturated character of organic compounds could be determined by addition reaction and be expressed with iodine value (National standards administration committee of China, 2008). When seedlac is bleached by sodium hypochlorite, the double-bond of its molecular structure is added by chlorine and inevitably vanished to some extent, which led to the decrease of the unsaturated double bond value (Ha and Wang, 1987). As a result the products shellac made from seedlac by bleaching becomes a hydrocarbon chloride shown in fig. 5 (b). With the removal of combined chlorine the unsaturated double bond value is restored (Liao *et al.,* 2009; Liao *et al.,* 2011). This could explain why the iodine value increases with the decrease of chlorine content after dechlorination by sodium ethoxide.

Bleached shellac, a natural product, can be used as enteric coating in pharmaceutical industry, but its consumption is inevitably decreased in this domain nowadays, because there exists combined chlorine in its molecule when it is manufactured. With the decrease of chlorine contained in the products the physicochemical properties (polymerization time and iodine value) of the products are modified better, and the shellac products with low combined chlorine could be used in pharmaceutical domains. In the alkyl halide molecule, because of strong absorption of halide atom, there is some positive charge not only at α carbon atom but at β carbon atom, and the density of electron cloud of β-C-H biases carbon atom. Hydrogen combined with β carbon atom shows lively and is susceptible to leave when it reacted with a strong

alkaline reagent because of electron inducing effects of halogen atoms. When alkyl halide reacted with alkaline under the conditions of aqueous solution, both alcoholate produced by substitution reaction and olefin produced by elimination of hydrogen halide are got (Pozniak and Kuliszewska, 2013). Moreover the products of mixed ether could be generated when alkyl halide reacted with nucleophilic reagent like alkaline reagents. But this is usually occurred by primary alkyl halides, and few of this kind of products is obtained by secondary alkyl halides, and the main products which resulted from the reaction between sodium alcoholate and tertiary alkyl halides are olefins not ether. The final products shellac bleached from seedlac by bleaching with sodium hypochlorite are mainly both secondary alkyl chloride and tertiary chloride. In terms of elimination of hydrogen halide in alkyl halide compounds, an atom (or group) is come off from two adjacent carbon atoms. That is to say, halogen atom is removed from α- carbon atom and hydrogen is off from the beta-atom. Correspondingly unsaturated bonds (C=C double bonds) are formed.

From the analysis mentioned above, when bleached shellac react with dechlorination agent, most of chlorine combined in adjacent carbon atoms in the cyclic terpene acid are eliminated largely on ways of eliminating reaction. In the dechlorination process, first and foremost the chlorine, in the form of tertiary alkyl chloride, which combined with carbon atom connecting the group of carboxyl in cyclic terpene acid is eliminated, and double bonds are formed in products. Then most of the chlorine adjacent is eliminated and removed and also double bonds are formed, and part of them are substituted by $-OC_2H_5$ by means of nucleophilic substitution which induce the formation of ether bonds. Accordingly there are different three kinds of structures in shellac when it is modified by dechlorination to eliminate chlorine combined in its molecule, which are shown in fig. 6.

CONCLUSION

From the experimental results and discussion mentioned above, it could be derived that with the decrease of chlorine combined in shellac iodine value increases correspondingly, and that shellac which has nearly the same iodine value as seedlac, raw materials for preparing shellac, could be got by means of dechlorination.

The structure of shellac made from seedlac by means of bleaching with sodium hypochlorite becomes an alkyl chloride with both secondary and tertiary chlorine, because chlorine is added in its double bond. The structures of shellac obtained by means of dechlorination are different from that of products without dechlorination. Combined chlorine contained in the shellac has great impacts on the physicochemical properties of shellac, especially on the unsaturated bond (expressed by iodine value) and polymerization time. The chlorine content is decreased effectively after the sodium ethoxide is added into alkaline bleached solution of seedlac to eliminate chlorine under the conditions of temperature 90□ for different time.

It is demonstrated by ultraviolet spectra of samples that the unsaturated C=C double bond of seedlac was added by chlorine when it was bleached with sodium hypochlorite and that most of the combined chlorine was removed by elimination reaction in the presence of sodium ethoxide.

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