Dissolution of Condensed Tannin with Phenol: Optimum Reaction Parameters and Some Flow Properties

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ABSTRACT: Condensed tannins from the bark of black wattle (*Acacia mearnsii* L.) were solubilized with phenol using HCl as a catalyst. The optimum reaction parameters (temperature, time, and acid concentration) of the dissolution were determined. The results showed a clear effect on the percentage of reacted phenol and residue tannin by temperature, time and, particularly, acid concentration. It was found that almost 77% of the phenol used could be reacted with the tannin, and about 90% of the tannin could be solubilized into phenol in the presence of HCl (as a catalyst) having a concentration of 5%. The optimum temperature, time, and acid concentration were 160°C, 90 min, and 4%–5%, respectively. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2450–2453, 2005

Key words: HCl; condensed tannin; dissolution; phenol; reaction parameters

INTRODUCTION

Condensed tannins are phenolic compounds consisting of several types of flavan-3-ols (afzelechin, gallocatechin, and catechins) and flavan-3,4-diols (leucopelargonidin, leucodelphinidin, and leucocyanidin; Fig. 1).[1,2] They are covalently bound to carbohydrate matrixes within plant cells. They can be extracted with hot water and solvent as well as by steaming. Condensed tannins exist in the barks of black wattle (*Acacia mearnsii* De Wild or *A. mollissima* L.), *Salix* spp., *Eucalyptus* spp. and some conifers such as *Picea* and *Pinus*, particularly, *Pinus brutia* Ten., as well as in the wood of quebracho (*Shinopsis* spp.).[3,4]

Thus far, many studies have investigated the replacement of phenol with tannins in tphenol-formaldehyde-type adhesives.[4–17] In addition, using tannin as polyol replacements in the production of polyurethane-type foams,[18–20] as well as an protein-adsorbing agent,[21] has been studied extensively by Sakai et al. in recent years.

Tannin has been found to be the best replacement for phenol in the production of phenol-formaldehyde-type adhesive (liquid form) because of its higher reactivity to formaldehyde. Specifically, tannin extracted from the bark of the black wattle and the wood of quebracho was commercialized in New Zealand, Australia, and South Africa for making hot- and cold-setting-type adhesives for the wood industry.[4–5,15]

Thus far, there have been some studies of the dissolution of condensed tannin with phenol in the presence of sulfuric acid (Fig. 2) in order to control the reactivity of phenol with formaldehyde in the presence of a basic medium,[15] as well as on several mechanisms of several acid-catalyzed dissolution of catechin.[22,23] More recently, Mutlu et al. reacted phenol-modified condensed tannin with formaldehyde to make polymer matrix for brake linings.[24] In the mean time, it was shown that lignocellulosic biomass such as wood and wheat straw could be dissolved with phenol by using acidic catalysts in order to make phenol-formaldehyde-type resin.[25] However, to our knowledge, no study has investigated the use of tannin as a replacement for phenol-formaldehyde-type resin, so-called novolak resin.

Therefore, the aim of the current study was to modify/dissolve condensed tannin extracts from the barks of black wattle using an acidic catalyst (HCl) and to determine the optimum dissolution parameters. In a future study, we will make molding materials from condensed tannin modified with phenol and characterize them.

EXPERIMENTAL

Materials

Tannin extracts from the bark of the black wattle (*Acacia mearnsii* L.) were provided from ALTIN Leather

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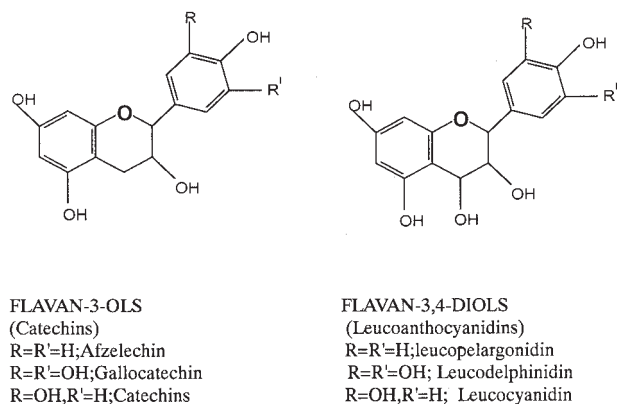*Correspondence to:* M. H. Alma (alma@ksu.edu.tr).

Figure 1 Several types of condensed tannins.

Co. (Kahramanmaras, Turkey). Phenol and 35% aqueous HCl were used as the main solvent and acidic catalyst, respectively, in the dissolution of tannin. 1,4-Dioxane was used as a solvent to dissolve the obtained reaction mixture. The chemicals were of reagent grade and used without further purification and were purchased from Merck (Germany).

Dissolution of condensed tannins with phenol

First, a mixture of oven-dried tannins from the bark of black wattle, phenol (phenol:tannin ratio of 2 : 1 by weight), and 35% HCl was heated in a two-neckedglass flask furnished with a condenser and a mechanical stirrer under atmospheric pressure at various temperatures and times.

And then the resulting reaction mixture was dissolved with 1,4-dioxane solvent and filtrated with a glass-fiber filter (Toyo GA-100). Finally, while the dioxane-insoluble parts, the so-called tannin residue, were mainly oven-dried and weighed, the dioxane-soluble parts that resulted were evaporated at 50°C under vacuum in order to remove the dioxane.

Determination of percentage of tannin residue

The percentage of tannin residue (the dioxan-insoluble part of tannin) was determined by dividing the amount of the oven-dry weight of 1,4-dioxane-insolu-
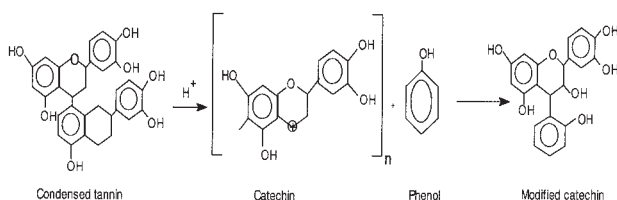

Figure 2 Hypothetical reaction between catechin and phenol in the presence of sulfuric acid.
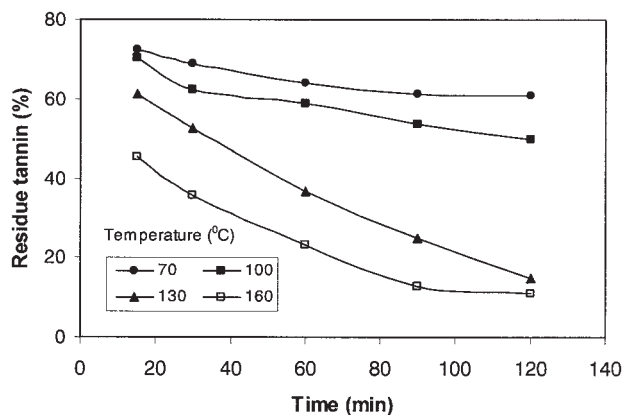

Figure 3 Relationship between reaction time and tannin residue, that is, the percentage of unsolubilized condensed tannin, as a function of reaction temperature (35% HCl concentration: 5%; phenol-to-tannin ratio: 2 : 1).

ble part of tannin by the oven-dry weight of the starting tannin.

Determination of percentage of reacted phenol

To determine the percentage of reacted phenol, the amount of free phenol remaining in the methanol-soluble part was first measured using high-performance liquid chromatography (HPLC; Cecil 1100 series) equipped with a UV–vis detector (280 nm) and a Zorbax ODS column (4.6 × 25 cm). Measurements were done at 30°C and a flow rate of 10 mL/min using a methanol/water solution [1 : 2 (v/v)] as the mobile phase. Moreover, phenol was used as a standard solution. For the measurements, the methanol-soluble part (2.5 μL) was injected into the HPLC apparatus. Then the percentage of reacted phenol was determined by dividing the amount of the reacted phenol by the total amount of the starting phenol.

Determination of melting point

The melting point was measured by using a digital melting point apparatus (BI 9200 Barnstead/Electrothermal (IA 9000 series; made in the UK/USA). For each trial, the average of three measurements is reported.

RESULTS AND DISCUSSION

Figure 3 indicates the relationship between reaction time and the percentage of tannin residue as a function of reaction temperature. It is clear from Figure 3 that the percentage of tannin residue decreased with an increasing reaction time. For example, when the reaction time increased from 15 to 120 min at 160°C, a decrease of about 35% was obtained. This tendency is
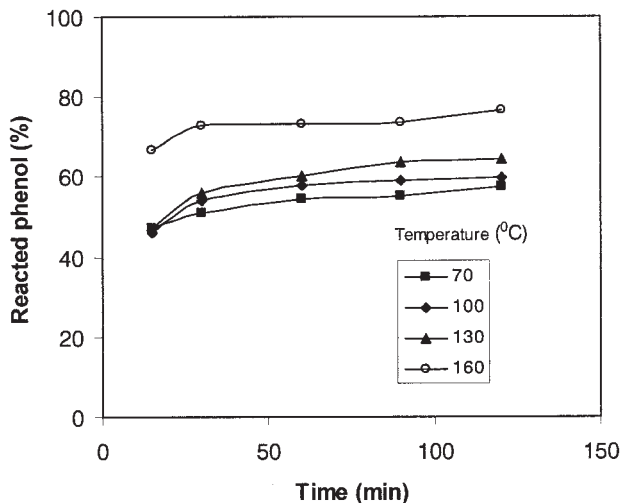
Figure 4 Relationship between reaction time and percentage reacted phenol as a function of reaction temperature (35% HCl concentration: 5%; phenol-to-tannin ratio: 2 : 1).

Figure 5 Relationship between HCl concentration and percentage of tannin residue, which is unsolubilized condensed tannin (phenol-to-tannin ratio: 2 : 1; reaction time: 60 min; reaction temperature: 70°C).

most drastic for reaction temperatures of 130°C and 160°C. Reaction temperatures of 70°C and 100°C produced almost the same percentage of tannin residue. The optimum reaction time for obtaining the smallest percentage of tannin residue (about 11%) was determined as being at 160°C for 90 min or at 130°C for 120 min. It is clear that reaction time was more effective at the higher temperatures studied, 130°C and 160°C, compared to the other two temperatures studied, 70°C and 100°C.

Figure 4 demonstrates the relationship between reaction time and percentage of reacted phenol as a function of reaction temperature. As can be seen from Figure 4, when reaction time increased from 15 min to 30 min, the percentage of reacted phenol linearly increased and then slowly increased with a further increase in the reaction time at all reaction temperatures. Moreover, Figure 4 also shows that difference in the percentage of reacted phenol was negligible at temperatures of 70°C, 100°C, and 130°C. Yet, when the reaction temperature increased from 130°C to 160°C, the percentage of reacted phenol increased considerably at all the reaction times studied. A maximum percentage of reacted phenol of as much as 77% could be obtained at 160°C and 120 min, whereas the lowest percentage of reacted phenol was 46%, obtained at 70°C and 100°C for 15 min. It can be concluded that the optimum reaction time and temperature were 60 min and 160°C, respectively, in order to get largest amount of reacted phenol and the smallest amount of tannin residue.

Figure 5 depicts the effects of 35% HCl concentration on the percentage of tannin residue. As indicated in Figure 5, the percentage of tannin residue sharply decreased with an increasing acid concentration when the HCl concentration increased from 1% to 4% and
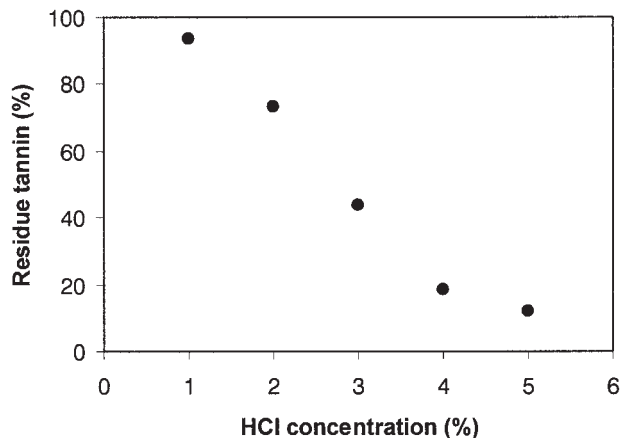
then slowly went down with further increases. About 90% of the condensed tannin was found to be dissolved in phenol at an HCl concentration of 5%.

The relationship between the HCl concentration and the percentage of tannin residue is illustrated in Figure 6, from which it is evident that, as for for relationship between acid concentration and residue tannin ratio, the percentage of reacted phenol linearly increased with an increasing acid concentration and then drastically increased with further increases in acid concentration. The optimum acid concentration was determined to be 4%–5% for obtaining the largest amount of reacted phenol and the smallest amount of tannin residue.

As is very well known, condensed tannin (see Fig. 1) shows a recondensation reaction in the presence of acid catalysis.[3] However, it was reported that when
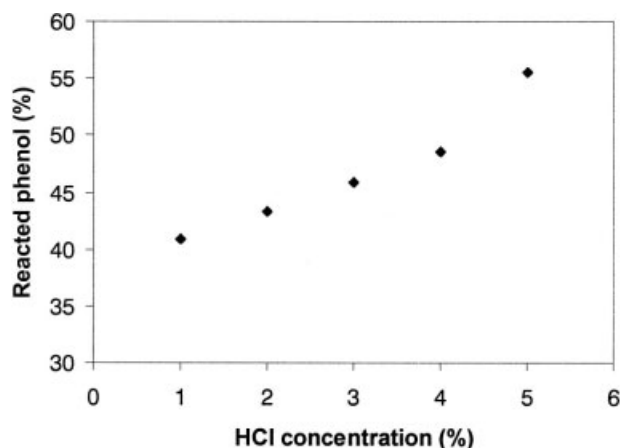

Figure 6 Relationship between HCl concentration and percentage of reacted phenol (phenol-to-tannin ratio: 2 : 1; reaction time: 60 min; reaction temperature: 70°C).
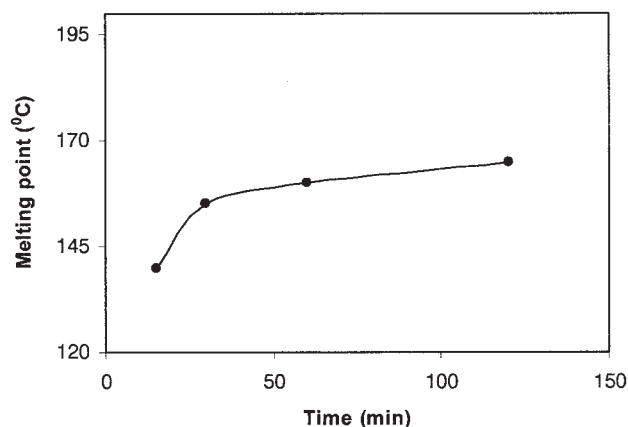
Figure 7 Relationship between reaction time and melting point (35% HCl concentration: 5%; phenol-to-tannin ratio: 2 : 1).

condensed tannin was dissolved in phenol in the presence of acid catalysis, no recondensation reaction occurred, meaning that phenol inhibited the condensation of tannin and reacted with cleaved components of the tannin like lignin.[4] Moreover, it was determined that the dissolved tannin components, such as catechin and afzelechin, bonded to phenol (also see Fig. 2).[5,23] Furthermore, it was found that when bark was dissolved in phenol under acid catalysis, phenolation took place, that is, bark components such as cellulose, lignin, and tannins bonded to phenol.[8]

Figure 7 shows the melting point of tannin modified with phenol as a function of reaction time, which indicated that the melting point linearly increased when time was increased from 15 to 30 min and then slowed down with additional increases. This phenomenon can be attributed to the increased percentage of reacted phenol at greater reaction times, a finding in agreement with data for wood modified with phenol.[25]

CONCLUSIONS

Condensed tannins from the bark of black wattle could be dissolved successfully with phenol in the presence of HCl as a catalyst. The percentage of reacted phenol and residue tannin were found to be dependent on temperature, time and, in particular, acid concentration. It also was determined that approximately 77% of phenol could be reacted with the tannin and about 90% of the tannin could be dissolved with phenol by using HCl with a concentration of 5%. The optimum temperature, time, and acid concentration were 160°C, 90 min, and 4%–5%, respectively.

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